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INORGANIC CHEMISTRY

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PREFACE

The volumes of the International Library of Technology are made up of Instruction Papers, or Sections, comprising the various courses of instruction for students of the International Correspondence Schools. The original manuscripts are prepared by persons thoroughly qualified both technically and by experience to write with authority, and in many cases they are regularly employed elsewhere in practical work as experts. The manuscripts are then carefully edited to make them suitable for correspondence instruction. The Instruction Papers are written clearly and in the simplest language possible, so as to make them readily understood by all students. Necessary technical expressions are clearly explained when introduced.

The great majority of our students wish to prepare themselves for advancement in their vocations or to qualify for more congenial occupations. Usually they are employed and able to devote only a few hours a day to study. Therefore every effort must be made to give them practical and accurate information in clear and concise form and to make this information include all of the essentials but none of the non-essentials. To make the text clear, illustrations are used freely. These illustrations are especially made by our own Illustrating Department in order to adapt them fully to the requirements of the text.

In the table of contents that immediately follows are given the titles of the Sections included in this volume, and under each title are listed the main topics discussed. At the end of the volume will be found a complete index, so that any subject treated can be quickly found.

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INORGANIC CHEMISTRY

(PART 1)

GENERAL DISCUSSION

DEFINITIONS AND LAWS

1. Chemistry is that branch of natural science which treats of the relations and combinations of atoms. It considers the properties of matter, the changes that affect its composition, and the numerous laws and theories governing these changes.

Inorganic chemistry treats of the elements and their compounds with the exception of those of the hydrogen-carbon type.

The Egyptians appear to have had a greater knowledge of chemistry than any of the ancient nations. They prepared many medicines and pigments as well as soap, vinegar, metals and metallic alloys, salt, glass, enamel, etc. The Chinese, also, were early acquainted with processes for dyeing and for making metallic alloys, niter, sulphur, gunpowder, borax, alum, and paper. The Romans obtained their knowledge of chemistry from the Egyptians and Greeks, but added little or nothing to this knowledge. Further study of chemistry was taken up by the Arabs and was carried on by them and by their European scholars. The first germs of the real science of chemistry appeared about the end of the 17th and the beginning of the 18th century, and after this chemistry advanced rapidly. At this time Margraff added alumina and magnesia to the then known earths, Priestley announced his discoveries of oxygen, Rutherford discovered nitrogen, and Scheele added chlorine.

Between 1770 and 1794 Lavoisier founded the system that still remains the framework of the science. Berthollet contributed much to the doctrine of affinity, and Berzelius made many researches in mineral chemistry. Many of his determinations of the atomic weights of the elements are still accepted as correct.

2. Matter.—It is rather difficult to give a satisfactory definition of the term *matter*, but in a general way it may be defined as anything that occupies space and possesses weight, or is acted on by gravitation. There are many kinds of matter; for example, the different kinds of rock, the various substances that compose vegetable and animal organisms, and the great number of manufactured products. Hence, **matter is anything that occupies space and possesses weight.**

3. Energy.—It might at first appear that the definition of matter just given is sufficiently extensive to embrace everything; but a little reflection will show that there is something besides matter. This something is known as *energy*, and it may be said that matter and energy compose the sensible universe.

A hammer occupies space and possesses weight, hence it consists of matter; but if a number of blows are struck with this hammer on a piece of iron, something is observed that is not matter. The hammer has not lost weight, nor has the iron gained any, and yet these blows must be something, for they produce certain effects. As the blows were delivered, the iron gave forth sound; it is altered in shape, and further, it has acquired temporary heat. Again, if the hammer head is carefully weighed, and then made red hot in a fire, it will weigh exactly the same as it did when cold. Further, if it is allowed to cool, it imparts heat to its surroundings, but still remains unaltered in weight. Here, then, is something very definite that is not matter. It is known as **energy**, which may be defined as *the capacity of a body for doing work*, the quantity of energy it possesses being measured by the work it can do.

There are different forms of energy, as, for example, motion, heat, light, electricity, etc., and under the influence of these

different forms, matter is constantly undergoing change. Changes in position and temperature are most frequently noticed, but other changes are continually taking place. Electrical changes are seen during electrical storms or thunder showers; magnetic changes are detected by means of the magnetic needle, and, finally, there are changes in the composition of substances, known as chemical changes. It is with the latter changes that the chemist is principally concerned.

4. Physical and Chemical Changes.—If a piece of platinum wire is heated in the flame of a Bunsen burner it soon becomes white hot and emits light and heat. Its physical condition is now very different from what it was before it was placed in the flame, but it is still platinum. This may be shown by removing it from the flame, when it will quickly cool and resume its silvery appearance. The heat has not permanently altered it in any way, not even tarnished it.

Now, if a piece of magnesium wire is heated in the same way, a remarkable action is observed. The wire burns with a peculiar dazzling white light and leaves a white, easily powdered substance composed of magnesium and oxygen, known as *magnesia*.

In the case of the platinum wire, the change is purely *physical*. The hot wire possesses properties very different from those it possessed when cold, but as soon as it cools it regains its original character, and at no time is it composed of anything but platinum. With the magnesium wire there is a *chemical action*; the silvery looking magnesium entirely disappears during the vigorous combustion, and a white, brittle substance is left in its place. Not a particle of metallic magnesium remains. It thus appears that *physical changes do not alter the composition of substances, but that chemical changes are changes in composition by which the identity of the substance itself is changed*. Changes of this kind are constantly taking place around us. If the sweet juice of apples is allowed to stand in the air, a chemical change takes place and the result is vinegar. If a flame is brought in contact with a little gunpowder, a chemical change takes place; there is a puff of smoke and the powder, as such, entirely

disappears. Practically the same thing occurs in all cases of combustion. These phenomena are so familiar that they no longer excite curiosity.

5. Molecules and Atoms.—In early times there were two views held in regard to the constitution of matter. One of these was that all matter was continuous and therefore capable of infinite subdivision—that there was no limit beyond which the division of matter could not be carried. According to the other theory, it was held that matter was composed of extremely small separate particles, and that subdivision could be carried on until these ultimate particles were reached, and beyond this, no further subdivision was possible, for these ultimate particles were regarded as indivisible. This latter view, somewhat modified, is the one universally adopted at the present time. This theory is incapable of direct proof, but as all the observed facts fit in, and as it is capable of explaining all related phenomena, the student of chemistry soon comes to accept it as a fact about which there is no doubt. The theory as accepted at present is as follows: If a portion of matter is subjected to a process of subdivision, there will finally be obtained an extremely minute particle that cannot be further subdivided by mechanical means. This is known as a *molecule*, and is the smallest portion of matter that retains the properties of the original substance. If chemical methods are now employed, this subdivision can be carried still further, the result being that the molecule is thereby resolved into its ultimate particles, or *atoms*, beyond which we are unable to carry the subdivision. A **molecule** may, therefore, be defined as *the smallest portion of matter obtainable by mechanical or physical subdivision, or the smallest particle of matter having the properties of the original substance*. The word **atom** means indivisible or undivided. In use, the term is applied to the smallest divisions of matter that can be obtained by the most refined methods at present known to the chemist. Hence, atoms are undivided, though possibly not indivisible; therefore, an **atom** is *the smallest particle of an element which can be obtained by chemical subdivision*. Keeping this in mind,

the definition of physical and chemical changes may be extended as follows:

A **physical change** is one that does not affect the molecule.

A **chemical change** is a change within the molecule.

6. Symbols and Formulas.—Each element has an abbreviation of its full name, called its **symbol**. These abbreviations usually consist of the initial letter of the Latin name of the element. As, however, there are about seventy elements, and only twenty-six letters in the alphabet, a large number of the symbols are composed of the initial and another distinctive letter selected from the name. Thus, the three elements carbon, chlorine, and copper (cuprum) all have names commencing with the letter C; carbon has the letter *C* for its symbol, while *Cl* and *Cu* stand for chlorine and copper, respectively.

As all compound bodies are the result of the combination of elements, they may conveniently be expressed symbolically by placing side by side the symbols of the constituent elements. The symbol of a compound is termed a **formula**. Therefore, a *formula is a group of symbols showing the composition of a compound*. Thus, common salt consists of sodium, whose symbol is *Na*, and chlorine, whose symbol is *Cl*; accordingly, *NaCl* is written for its formula.

The multiplication of atoms is expressed by placing an Arabic numeral in front of the symbol; the number of atoms of the same kind in a molecule is represented by placing an Arabic numeral to the right of and below the symbol; thus, $3S$ means merely 3 atoms of sulphur, H_2 means 1 molecule of hydrogen consisting of 2 atoms. The multiplication of a molecule is usually expressed by placing an Arabic numeral in front of the formula, but sometimes by enclosing the formula in parentheses and placing the numeral to the right of and below it. Thus, $2H_2O$ and $(H_2O)_2$ both mean 2 molecules of water, but the former is nearly always used. Groups of atoms that act as single atoms are usually enclosed in parentheses and the numeral placed at the right of and below the formula. Thus, $(OH)_2$ means two groups, each composed of 1 atom of hydrogen and 1 atom of oxygen.

The elements have obtained their names in a variety of ways. It would be difficult to trace the derivation of many of the names, but with others this is very simple. Some of them derived their names from the country in which they were discovered. Thus, germanium was discovered in Germany, gallium in France, columbium in America, etc. Some derived their names from some peculiar property. Thus, chlorine derived its name from the Greek name of its color; bromine from the Greek word for stench; cæsium, which is the Latin name for sky blue, from the blue lines that characterize this element's spectra, etc.

7. Compounds and Elements.—Experiments have shown that by far the greater number of substances with which we are familiar may be decomposed into simpler substances. For example, if a little mercuric oxide is heated in a test tube, it is decomposed into two substances—mercury and oxygen. It may be shown by experiment that the combined weights of the mercury and oxygen obtained are exactly equal to the weight of the mercuric oxide decomposed. Furthermore, if the mercury and oxygen are brought together again under proper conditions they will unite, forming exactly the amount of mercuric oxide previously decomposed. It appears, then, that mercuric oxide is composed of at least two simpler substances, mercury and oxygen, into which it can be resolved by proper chemical methods. The same may be said of by far the greater number of known substances. On the other hand, there are a number of substances that the most refined methods known to the chemist have failed to decompose. Mercuric oxide is resolved into two simpler substances by the mere application of heat, but no treatment has ever succeeded in producing anything simpler than mercury from mercury, or anything simpler than oxygen from oxygen. Whether or not these are capable of being decomposed is not known. All that can be said positively is that with his present knowledge and the appliances at his command the chemist is unable to decompose them into anything simpler. The substances that can be decomposed into simpler ones are known as **compounds**.

Those that cannot be decomposed into anything simpler are known as **elements**. There are about 83 substances at present that cannot be decomposed, and are therefore classed as elements. The exact number of elements cannot be given, as there are indications that some of the substances usually thought to be elements are composed of more than one substance, and it is probable that there are still some undiscovered elements.

All the various forms of matter that come within our knowledge are composed either of these single elements or of combinations of them. About a dozen of these elements are quite common, and the rest are comparatively rare. Most of the substances with which we are familiar are composed of some of these common elements. Some compounds, like mercuric oxide, are composed of two elements, others contain a greater number, but most compounds are simple, and comparatively few contain more than four or five elements.

8. Mechanical Mixtures and Chemical Compounds.

It was stated in the preceding article that all the substances with which we are familiar are made up of combinations of the elements; but combinations may be of two kinds: mechanical mixtures and chemical compounds. This may be nicely illustrated by certain pieces of limestone containing quartz crystals. It is very evident in this case that the stone contains two kinds of matter, and by carefully breaking it up and picking out the different kinds of matter, two distinct substances are obtained. They are limestone and quartz. As these substances are easily separated by mechanical means, it is evident that this is a mechanical mixture. Further mechanical treatment will have no effect on the constituents of the stone thus separated, but if the proper chemical methods are employed, each of these constituents can be resolved into its constituent elements. The quartz is composed of silicon and oxygen, and the limestone of calcium, carbon, and oxygen. Hence, the original stone was a mechanical mixture of two chemical compounds, composed of the elements calcium, carbon, silicon, and oxygen.

Again, if fine copper filings and sulphur are placed together in the proper proportions and mixed thoroughly, the mixture

will have properties different from either copper or sulphur; the color is somewhat greenish, and to the unaided eye it might appear to be a homogeneous substance. The properties of the mixture may broadly be said to be a mean of the properties of copper and sulphur. If, however, a little of the mixture be examined under the microscope, the particles of copper and sulphur may be distinctly seen lying, unaltered, side by side. Furthermore, if part of the mixture is treated with carbon bisulphide, the sulphur will dissolve in it and leave the copper in its original condition. If this solution is evaporated, the sulphur will be left unchanged. In another portion of the mixture the copper and sulphur may be separated by taking advantage of their difference in density. All these experiments show that the copper and the sulphur merely form a mechanical mixture.

If, now, the remainder of the mixture is placed in a test tube and heat is applied, it will soon begin to glow, and it becomes evident that a serious change is taking place. If it is removed from the flame it will continue to glow until every particle of the mixture has been changed, the reaction growing more vigorous as it proceeds. If, when cool, the substance is removed from the tube, instead of being the yellowish-green powdered mixture, it will be found that it is a black, homogeneous, brittle solid. Examined under the microscope, it shows no trace of either copper or sulphur. Carbon bisulphide does not dissolve the sulphur. No physical treatment can separate it into its constituents. In fact, all the properties are changed; a chemical change has taken place, and a new compound, copper sulphide, is formed.

If the experiment was carefully performed, and proper precautions observed, it will be found that the copper sulphide formed weighs exactly the same as the mixture of copper and sulphur heated, showing that nothing is either gained or lost during the reaction. It will also be noticed that although the test tube is removed from the flame as soon as the mixture begins to glow, the action proceeds and becomes more vigorous, showing that the reaction is generating more than enough heat to carry on the reaction. It will be observed later that all

chemical reactions are accompanied by either an evolution or absorption of heat. These observations, however, are more or less aside. The principal thing to be observed at this point is the difference between the mechanical mixture of copper and sulphur, and the chemical compound, copper sulphide.

From these examples it may be readily seen that a mechanical mixture is a collection of substances, either elements or compounds, which retain their original identity, and which may be separated by mechanical means. A chemical compound, on the other hand, is made up of elements so combined that each has lost its original identity, and whose properties have been changed either with an evolution or an absorption heat, and which cannot be separated except by chemical action.

D. Forms of Matter.—Bodies exist in three forms or conditions: *solid*, *liquid*, and *gaseous*. It is a well-established theory that molecules are in a constant state of motion, and it is also generally accepted as a fact that molecules attract one another through short distances. This attractive force is called *cohesion* in the case of like, and *adhesion* in the case of unlike, molecules. When the molecules are close together, the attractive force is strong, and there is but comparatively little motion among the molecules, the substance is a *solid*. If there is greater freedom of motion among the molecules and the attraction is less but still sufficient to hold them together loosely, the body is a *liquid*. If the motion of the molecules among themselves becomes so great that the attractive force is nearly overcome, the molecules appear to repel one another and fly apart, filling every portion of the space allotted to them, the body is a *gas*. One body may assume all three forms at different temperatures. For instance, in the case of ice there is but comparatively little freedom of motion among the molecules; they are comparatively close together, and the attractive force is strong. The result is the *solid*—ice. If heat is applied, the molecular motion is increased, the molecules being driven further apart; the attractive force becomes less, and there is great freedom of motion among the molecules. The result is the *liquid*—water. If, now, the heat is continued, the vibration

of the molecules becomes greater, until the attractive force is entirely overcome and the molecules repel one another, flying apart and filling every portion of the space allotted to them. The result is the gas—steam. The repulsive force is only apparent in the case of gases, but many chemists think it is also present in the case of solids and liquids, and explain the three forms of matter by saying that in a solid the attractive force predominates, in a liquid the forces of attraction and repulsion are about evenly balanced, and in the case of gases the repulsive force predominates.

10. Electrolytic Dissociation.—When a current of electricity is passed through a solution of hydrochloric acid, chlorine is given off at the positive pole and hydrogen at the negative pole. According to the old theory, this was due to a tearing apart of the molecules by the electric current. Many facts, however, make it probable that this decomposition is not actually brought about by the electric current, but that the ions of chlorine and hydrogen exist already separated in the solution. **Ions** are not atoms but are electrically charged atoms or groups of atoms. Hence, a dilute solution of hydrochloric acid contains not only molecules of hydrochloric acid but also a large proportion of separated, electrically charged ions of hydrogen and chlorine, and since these ions are electrically charged, the dissociation is called **electrolytic dissociation** or **ionization**.

According to the present theory of electrolytic dissociation, the greater number of salt molecules in a strong solution are unaltered, but some of them are dissociated into their ions. When the solution is diluted the dissociation progresses rapidly, and in a very dilute solution nearly all the salt is present in the form of ions. Each ion is supposed to bear a charge of electricity, an electropositive ion having a positive charge, while an electronegative ion has a negative charge. These charged ions cannot escape from the solution without giving up their charges of electricity to some oppositely charged body. This happens at the poles of an electrolytic cell during electrolysis. Thus, when a dilute solution of sodium chloride is said to contain free

ions of sodium and chlorine it must not be supposed to contain free sodium and free chlorine. What are actually present, however, are positively charged ions of sodium and negatively charged ions of chlorine. During electrolysis the negatively charged ions of chlorine give up their negative charges at the positive pole and escape as free chlorine, while the sodium gives up its positive charges at the negative pole.

One of the most important arguments in favor of this view is afforded by the fact that almost all the properties of such dilute solutions have been shown to be equal to the sum of the properties of the ions. Each ion has a definite weight, volume, color, etc., and the effect produced by a salt is found to be equal to the sum of the effects independently produced by the separate ions. This theory is in accordance with the physical properties of dilute solutions, and throws great light on many chemical reactions. According to this view, chemical action in dilute solutions takes place between the ions of the substances concerned. Hence, tests usually applied for the metals and acids are really tests for the corresponding ions. This accounts for the fact that tests for ferrous salts fail in the case of potassium ferricyanide, although they are perfectly satisfactory with ferrous sulphate. This is due to the fact that in the case of ferrous sulphate the ferrous iron ion is present; whereas, in the case of potassium ferricyanide, the ions are potassium and a complex ion having the formula $Fe(CN)_6$.

11. Indestructibility of Matter. When a reaction takes place between substances nothing is gained or lost. The products of the reaction will weigh the same as the constituents entering into the reaction. For instance, when mercuric oxide is heated, the weight of mercury and oxygen produced is exactly equal to the weight of mercuric oxide heated; when copper and sulphur are heated together, the copper sulphide formed weighs exactly the same as the copper and sulphur taken. In every case in which this has been tried, the product weighed exactly the same as the constituents. Hence, we are justified in concluding it is so in every case. If not carefully studied, many natural phenomena might lead to the opposite conclusion. For

instance, a tiny seed dropped in the ground springs up and grows to a majestic tree. Here matter seems to have sprung into being, but if carefully examined it will be found that the tree has grown solely by material absorbed from the soil and air. After a time the tree is hewn down and burned, and all that remains visible of the tree is a little pile of ashes. Here matter appears to have been destroyed, but if the gases escaping from the combustion were collected, it would be found that not a particle of matter was lost. Up to Lavoisier's time, chemists seem to have tacitly held that matter could be destroyed, but by the use of the balance this chemist showed that when matter is apparently destroyed, it continues to exist in some other form. By many experiments, Lavoisier established the law of the indestructibility of matter, and established the quantitative method of studying chemical phenomena, thus laying the foundation of modern chemistry. The law of the indestructibility of matter is usually stated as follows:

The weight of the resulting compounds is invariably equal to the sum of the weights of the bodies entering the reaction.

According to this law, if it has always held good (and we believe that the laws of nature are unchangeable), there is exactly the same amount of matter in the universe today that there was in the beginning, and there will be the same amount throughout all ages.

12. Conservation of Energy.—Just as matter can neither be created nor destroyed, so it is generally believed, at the present time, that the total amount of energy in the universe remains unchanged. Energy may be changed from one form to another, but a large number of painstaking experiments have tended to show that energy can neither be created nor destroyed. Chemical energy may be transformed into heat, or heat into chemical energy, etc. By burning a certain amount of a substance, a certain definite amount of heat is produced; this heat will produce a certain definite amount of motion, which may be made to produce a definite amount of electrical energy, and this, in turn, may be made to produce a certain definite amount of chemical change. Thus, it is

seen that energy is readily changed from one form to another, but a given amount of one form of energy always produces a corresponding amount of another form, so that the total amount of energy remains unchanged. Transformations of energy, like transformations of matter, are constantly taking place around us, but with energy, as with matter, it is believed that not the least particle is ever created or destroyed.

13. Law of Definite Proportions.—In an experiment previously described, it was noted that when copper and sulphur are heated together, copper sulphide is formed. Whether or not the elements always united in the same proportion to form a compound was a question that was not settled until the early part of the last century, and is one that can be settled only by a quantitative study of the process of formation of compounds. To study this question in the case of copper and sulphur, the elements would be mixed in various proportions and heated out of contact with air, and the mass examined to see if any of either element remained unchanged. The compound formed would also be decomposed and examined in each case to see whether the elements were present in the same proportion in the compound in every case. A great many compounds have been examined in this way from time to time, and about a quarter of a century ago Blas carried out a series of experiments, the most accurate chemical experiments ever performed to determine the accuracy of this law. In no case has there been any variation in the composition of the compounds prepared that could be detected by the most refined methods of analysis. As a large number of compounds have been examined and no variation in composition has ever been found to occur, the theory that elements unite in definite proportions is called a law and is generally stated as follows:

A chemical compound always contains the same constituents in the same proportion by weight.

This case is a good illustration of the way in which chemical laws are arrived at. A few compounds were examined and were found to be formed by definite proportions of the elements composing them; hence, the hypothesis of definite proportions

was proposed. More compounds were examined and the hypothesis was confirmed by all results obtained, and was consequently called a theory. After a great number of experiments were performed, and the theory was found to accord with all related facts and accepted theories, it was termed a law.

14. Law of Multiple Proportions.—The study of chemical combination had not proceeded very far until it was discovered that the same elements may unite in more than one proportion, forming different compounds. Thus, carbon and oxygen form two compounds, iron and sulphur form three compounds, and nitrogen and oxygen form five compounds. By a study of such cases in the early part of the last century, Dalton arrived at facts that led him to formulate the hypothesis of multiple proportions, which has since become one of the fundamental laws of chemistry. He first studied the two compounds of carbon and hydrogen, ethylene and methane, and found that they contained:

Ethylene, C_2H_4 , hydrogen 14.3 per cent., carbon 85.7 per cent.
Methane, CH_4 , hydrogen 25 per cent., carbon 75 per cent.

By comparing these figures he found that the ratio of carbon to hydrogen in ethylene is as 6 to 1, and in methane as 6 to 2, or that the weight of hydrogen combined with a given weight of carbon is twice as great in the case of methane as in ethylene. He then examined carbon monoxide and carbon dioxide and found that they contained:

Carbon monoxide, CO ,
carbon 42.86 per cent., oxygen 57.14 per cent.
Carbon dioxide, CO_2 ,
carbon 27.27 per cent., oxygen 72.73 per cent.

By comparing, he found the ratios of carbon to oxygen in the two compounds to be:

Carbon monoxide, 6 : 8
Carbon dioxide, 6 : 16

That is, the weight of oxygen combined with a given weight of carbon is twice as great in the case of carbon dioxide as in carbon monoxide. Further, if in the five compounds of nitro-

gen and oxygen such weights of the compound be taken as contain the same weight of nitrogen, the weights of oxygen will be proportional to the numbers 1, 2, 3, 4, and 5. Thus:

Nitrous oxide, N_2O ,	13.91 parts N, 7.94 parts O
Nitric oxide, NO ,	13.91 parts N, 15.88 parts O
Nitrogen trioxide, N_2O_3 ,	13.91 parts N, 23.82 parts O
Nitrogen peroxide, NO_2 ,	13.91 parts N, 31.76 parts O
Nitrogen pentoxide, N_2O_5 ,	13.91 parts N, 39.70 parts O

From investigating a number of cases like these, Dalton discovered the law of multiple proportions, which may be stated as follows:

When two elements form more than one compound with each other the weights of one that unite with a fixed weight of the other bear a simple ratio to each other.

15. Significance of the Laws of Proportion.—The announcement of the laws of definite and multiple proportions naturally leads to the questions: Why do the elements unite in definite proportions? When two elements form more than one compound, why do the weights of the elements entering the compounds form simple ratios? What is the meaning of the weights to which the elements combine? If the hypothesis that matter is continuous and infinitely divisible is held, it would be difficult to assign any cause for the union of the elements in definite proportions, but if the atomic theory is accepted the explanation is not difficult to find. It is believed that there is a large space between the atoms, and if such is the case, and the atoms have definite weights, combination of atoms would naturally take place in definite proportions. The law of multiple proportions is also explained by the atomic theory, for if all atoms of the same kind have the same weight, and the atoms of two elements A and B unite to form different compounds, they must form compounds having 1 atom of A and 1 atom of B, 2 atoms of A and 1 of B, 1 of A and 3 of B, 2 of A and 2 of B, or in some such manner, in any of which combinations the weights will bear a simple relation to each other. It is thus seen that the laws of definite and multiple proportion are in perfect harmony with the atomic

theory, and it appears that the combining weights must coincide with, or bear a close relation to, the weights of the atoms.

16. Atomic Weights.—It would obviously be out of place at this time to discuss the methods of obtaining the atomic weights of the elements, and this will consequently be treated later. A little reflection will show that the atoms are much too small to have their absolute weights determined, and consequently a standard is selected, and the relative weights of the elements as compared to this standard are taken as their atomic weights. In other words, *the atomic weight of an element is the relative weight of an atom of an element compared with that of an atom of hydrogen*. As hydrogen is the lightest known element, it was chosen as the standard and its weight called 1. If all the elements formed compounds with hydrogen, the determination of their atomic weights would be a comparatively simple matter, but unfortunately only a relatively small number of the elements unite directly with hydrogen. In the case of elements like chlorine that unite directly with hydrogen, the combining weight is easily obtained, for if 1 gram of hydrogen unites with chlorine, forming 36.46 grams of hydrochloric acid, $36.46 - 1 = 35.46$ grams of chlorine must have united with 1 gram of hydrogen, and if they united atom for atom forming HCl , then an atom of chlorine must be 35.46 times as heavy as an atom of hydrogen, or the atomic weight of chlorine is 35.46. Further investigations have shown this to be the correct atomic weight of chlorine. As hydrogen does not unite directly with many of the elements, but oxygen unites with nearly all of them, the ratio of oxygen to hydrogen was determined, and the oxygen compounds of the elements were examined in much the same manner as the hydrogen compound of chlorine just described, and the weights calculated, considering oxygen as 16 times as heavy as hydrogen, and in this way a false standard has been established. Quite recently, a long series of painstaking experiments has shown that oxygen is 15.88 times as heavy as hydrogen, instead of 16 times, and consequently all atomic weights based on the examination of oxygen compounds were erroneous. As oxygen compounds have been used in most

cases, it was proposed to consider the atomic weight of this element as 16 and perpetuate this error. After considerable argument on both sides of this question, the matter was submitted to a vote of the leading chemical societies of the world. It seems that a majority of individuals favored the retention of 16 as the standard, but a majority of the societies favored the adoption of $O=16$, and atomic weights based on this standard are now generally called international atomic weights. As the international atomic weights are the ones most frequently used, they will be used in these Sections. As atomic weights based on both standards are sometimes used, atomic weights based on each standard are given in Table I. This table gives the latest and most accurate atomic weights obtainable for the substances now generally believed to be elements. It is not unlikely that the list may be changed in the future, as some of the substances included may not be elements, and some of the atomic weights are almost certain to be changed, as there has not been enough careful work done on some of the rarer elements to insure accuracy; but, as previously stated, these are the most accurate weights obtainable at present. It will be noticed that the weights are not all carried to the same number of decimal places. This is because the degree of accuracy of the atomic weight determinations of the various elements varies. In the table given, the results are carried to the last significant figure.

As a further precaution, two of the elements—mercury and bismuth—were heated by oxygen, hydrogen, chlorine, bromine, iodine, carbon, sulfur, krypton, neon, xenon, and argon. The solid elements are solids; but at various temperatures all have been liquefied, with the exception of bismuth, which so far has been only slightly softened with the highest temperature that can be obtained.

17. Determination of Atomic Weights.—The atomic weight of an element, as already stated, is the number expressing the relation of the weight of an atom of a given element to the weight of an atom of some element chosen as a standard.

TABLE I—(Continued)

Name	Symbol	Atomic Weight		
		O = 16	H = 1	Approximate
Scandium.....	Sc	44.1	43.8	44
Selenium.....	Se	79.2	78.6	79
Silicon.....	Si	28.3	28.1	28
Silver (argentum).....	Ag	107.88	107.08	108
Sodium (natrium).....	Na	23.00	22.83	23
Strontium.....	Sr	87.63	87.0	87.5
Sulphur.....	S	32.07	31.83	32
Tantalum.....	Ta	181.5	180.2	181.5
Tellurium.....	Te	127.5	126.6	127.5
Terbium.....	Tb	159.2	158.02	159
Thallium.....	Tl	204.0	202.5	204
Thorium.....	Th	232.4	230.7	232
Thulium.....	Tm	168.5	167.26	168.5
Tin (stannum).....	Sn	119.0	118.1	119
Titanium.....	Ti	48.1	47.7	48
Tungsten (wolfram).....	W	184.0	182.6	184
Uranium.....	U	238.5	236.7	238.5
Vanadium.....	V	51.0	50.6	51
Xenon.....	Xe	130.2	129.24	130
Ytterbium (neoytterbium).....	Yb	172.0	170.7	172
Yttrium.....	Yt	89.0	88.3	89
Zinc.....	Zn	65.37	64.88	65
Zirconium.....	Zr	90.6	89.9	90.5

One method of selecting the atomic weight has been described in the case of chlorine (Art. 16). Atomic weights can be determined also by analysis when the proportion in which the atoms combine to form a molecule of the compound analyzed is known. Thus, 66.434 grams of silver chloride are formed by burning 50 grams of silver in chlorine. Now, it is known that

1 atom of silver unites with 1 atom of chlorine to form silver chloride, and since the atomic weight of chlorine is 35.46, the calculated atomic weight of silver is obtained thus:

$$66.434 - 50 = 16.434$$

which is the weight of the chlorine used. Then,

$$50 : 16.434 = x : 35.46, \text{ and } x = 107.88$$

the atomic weight of silver.

The approximate atomic weight of solids can be checked by the **law of specific heats** announced by Dulong and Petit. This is that *the product of the specific heat and atomic weight of the solid elements is a constant quantity.*

By **specific heat** is meant the quantity of heat necessary to raise the temperature of the substance 1 degree compared with the quantity of heat necessary to raise the temperature of the same weight of water 1 degree. The constant quantity obtained by multiplying the specific heat by the atomic weight is approximately 6.25, as will be found by averaging the products shown in Table II.

TABLE II
SPECIFIC HEAT CONSTANT

Element	Specific Heat	Atomic Weight	Product
Alumina.....	.0308	208.0	6.40
Cobalt.....	.1067	58.97	6.29
Copper.....	.0968	63.57	6.15
Iron.....	.1138	55.84	6.35
Nickel.....	.1092	58.68	6.41
Sulphur.....	.1844	32.07	5.91

This use of the law is illustrated as follows: The specific heat of silver is .0570, and this divided into 6.25 gives the approximate atomic weight of silver as 109. This agrees very closely with 107.88, the true atomic weight. This law has been of great assistance in determining the atomic weight of several elements, as, for example, that of uranium, which was finally accepted as 238.5 instead of 110.25. Both of these values agree with analyses, but the former conforms to the law of specific heat.

18. The plan followed in determining the atomic weight of zinc illustrates clearly the methods actually used in determining the atomic weights of the solid elements.

1. Hydrochloric or sulphuric acid is allowed to act on zinc, liberating hydrogen, and if a known weight of zinc is used, the weight of zinc necessary to liberate 1 gram of hydrogen is easily calculated. This number is the equivalent of zinc, and since 1 atom of zinc replaces 1 atom of hydrogen, then the ratio of the atomic weight of zinc to the atomic weight of hydrogen will be the same as the weight of zinc to the weight of hydrogen. According to this, the equivalent of zinc is 32.685, and thus far its atomic weight.

2. When zinc and hydrochloric acid react together, zinc chloride is formed. On analysis, the proportion of zinc to chlorine is found to be about 32.685 to 35.46. Now, assuming the elements to combine atom for atom and that the atomic weight of chlorine is 35.46, the atomic weight of zinc is 32.685.

3. Zinc oxide is formed when zinc is burned in air, and when this compound is analyzed the proportion of zinc to oxygen is 65.37 to 16. Hence, if the elements combine atom for atom the atomic weight of zinc is 65.37.

According to these three determinations zinc has the atomic weight of 32.685 or 65.37. The assumption has been that the elements unite atom for atom, but this assumption must be incorrect, because zinc, like all other metals, can have but one atomic weight. If the atomic weight of zinc is taken as 32.685, then zinc oxide must be composed of 1 atom of oxygen and 2 atoms of zinc; whereas, if the figure 65.37 is used, zinc chloride must consist of 1 atom of zinc and 2 atoms of chlorine, and 2 atoms of hydrogen must have been replaced by 1 atom of zinc.

Determined by the vapor-density method, which is described in *Organic Chemistry*, Part 1, the weight of a molecule of zinc chloride was found to be 133. Now, if zinc chloride consists of 2 atoms of chlorine and 1 atom of zinc, and the atomic weight 65.37 is used, its molecular weight is 136.3. Hence, the assumption regarding the number of atoms in zinc chloride is probably correct. However, there is no absolute certainty whether the

zinc in zinc chloride is not 1 atom weighing 65.37 or whether it is 2 atoms each weighing 32.685. The approximate atomic weight determined by applying the law of specific heats is found to be (6.25 divided by 0.094) 66.4. Hence, this shows clearly that the atomic weight of zinc must be 65.37.

19. **Atomicity.**—Some elemental molecules are composed of more than one atom. The number of atoms thus composing a molecule is found by dividing the weight of its molecule by its atomic weight. Thus, the weight of a molecule of chlorine is 70.92 and its atomic weight is 35.46; hence, the chlorine molecule contains two atoms, or it is said to be **diatomic**. Again, the weight of a molecule of arsenic is 299.84 and its atomic weight is 74.96; it therefore has an atomicity of 4, or is said to be **tetratomic**. An elemental molecule is called *monatomic*, *diatomic*, *triatomic*, *tetratomic*, or *hexatomic* according as its atomicity is 1, 2, 3, 4, or 6.

The accompanying list shows the atomicity of some of the elemental molecules:

<i>Monatomic:</i>	Krypton	Chlorine
Lithium	Neon	Indium
Potassium	Xenon	Bromine
Sodium	Chlorine	Tellurium
Rubidium	Bromine	Iodine (below 1,000° C.)
Cesium	Iodine	Sulphur (above 800° C.)
Glucinum	Fluorine	Selenium (above 1,200° C.)
Barium	Antimony	Aluminum
Strontium	Bismuth	<i>Triatomic:</i>
Calcium	Thallium	Ozone
Magnesium	Nickel	Selenium (below 800° C.)
Mercury	Copper	<i>Tetratomic:</i>
Zinc	Palladium	Phosphorus
Cadmium		Arsenic
Silver	<i>Diatomic:</i>	Vanadium
Gold	Hydrogen	
Lead	Nitrogen	
Argon	Oxygen	<i>Hexatomic</i>
Helium	Fluorine	Sulphur (about 500° C.)

The atomicity of the elements given in the list have been determined experimentally. An uncertainty exists as to the atomicity of antimony, bismuth, and thallium, owing to the fact

that the densities of these elements at from $1,600^{\circ}$ to $1,700^{\circ}$ C. are greater than those required for monatomic molecules, but less than the numbers corresponding to a diatomic molecule.

Sodium and potassium have been determined only approximately, as the vapors of these metals attack the apparatus. The results obtained, however, point to the conclusion that these elements are monatomic. The general result of the determination of the molecular weights of many of the metals render it probable that in nearly all cases the molecules are identical with the atoms. Experiments on nickel, gold, copper, palladium, magnesium, lead, and calcium have shown that the molecular weights of these metals are the same as the atomic weights. The numbers obtained for indium and aluminum, however, tend to indicate that these metals are diatomic.

20. Attraction of Atoms.—Most atoms have a strong attraction for one another, and are nearly always found in combination with other atoms of the same or different kinds. This force is usually called **chemical affinity**. As a rule, the more dissimilar the substances, the stronger the attraction of their atoms for one another, but if atoms of different kinds are not present, atoms of the same kind combine among themselves. Thus, 2 atoms of hydrogen unite to form a molecule of hydrogen, 2 atoms of chlorine to form a molecule of chlorine, etc. If, however, the hydrogen and chlorine are mixed in the sunlight, the molecules of the hydrogen and of the chlorine are broken up, and each atom of hydrogen unites with an atom of chlorine, usually with an explosion. Here the attraction of the dissimilar atoms of hydrogen and chlorine is so much greater than their attraction for atoms of the same kind that the molecules of hydrogen and chlorine are broken up and the dissimilar atoms unite with explosive violence. This attractive force acts only through very short distances, and it is believed that the atoms within the molecule are in a constant state of vibratory motion; hence, heat, by increasing the length of the vibrations, in many cases drives the atoms so far apart that the attractive force ceases to act, and the compounds are thus broken up. We thus see how heat serves to decom-

pose compounds. There are some exceptions to these rules, however. Some atoms exist alone, and seem to have no attraction for other atoms of the same kind, and in some cases but little attraction for dissimilar atoms under ordinary conditions. Active atoms are sometimes caused to exist in the uncombined condition for an instant. They are then said to be in the *nascent state*. This means that the atoms are not only uncombined, but are just ready to unite with other elements.

21. Molecular Weights.—As molecules are made up by the combination of atoms, it is obvious that the weight of a molecule is the sum of the weights of the atoms composing it; or, in other words, the molecular weight is the sum of the atomic weights of the constituent elements. Thus, the molecular weight of water, H_2O , is $2+16=18$. That is, 2 atoms of hydrogen each having an atomic weight of 1, and 1 atom of oxygen having an atomic weight of 16, form a molecule of water having a molecular weight of 18. Thus, H_2O , wherever seen, stands not only for 1 molecule of water, but for 18 parts by weight of water.

EXAMPLE 1.—What is the molecular weight of sodium chloride having the formula $NaCl$?

SOLUTION.—From Table I, $Na=23$ and $Cl=35.46$; then,
 $23+35.46=58.46$. Ans.

EXAMPLE 2.—What is the molecular weight of sodium hydrate having the formula $NaOH$?

SOLUTION.— $Na=23$, $O=16$, and $H=1.008$; then,
 $23+16+1.008=40.008$. Ans.

EXAMPLE 3.—What is the molecular weight of iron pyrite having the formula FeS_2 ?

SOLUTION.— $S=32.07 \times 2=64.14$ and $Fe=55.84$; then,
 $64.14+55.84=119.98$. Ans.

EXAMPLE 4.—What is the molecular weight of sulphuric acid, whose formula is H_2SO_4 ?

SOLUTION.— $H=1.008 \times 2=2.016$, $S=32.07$, and $O=16 \times 4=64$; then,
 $2.016+32.07+64=98.086$. Ans.

EXAMPLES FOR PRACTICE

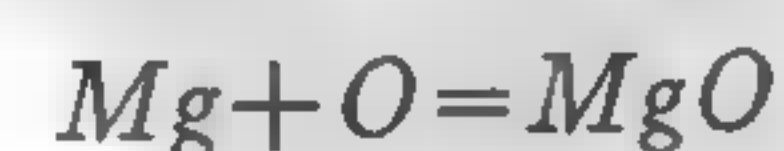
1. What is the molecular weight of a compound having the formula $Ba(OH)_2$?
Ans. 171.386
2. Determine the molecular weight of lead chromate, $PbCrO_4$.
Ans. 323.10
3. What is the molecular weight of: (a) Ethyl alcohol, C_2H_5OH ?
(b) potassium ferricyanide, $K_3Fe(CN)_6$? (c) potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$; (d) magnesium ammonium sulphate, $Mg(NH_4)_2(SO_4)_2$?
Use the approximate atomic weights.

Ans. $\begin{cases} (a) 46 \\ (b) 329 \\ (c) 422 \\ (d) 252 \end{cases}$

22. Equations.—When chemical action takes place, it is frequently desirable to represent what takes place by means of symbols and formulas, and as every chemical change or reaction is simply an alteration in the association and position of atoms, and consequently a change in the composition of the molecules, it is obvious that chemical reactions may be represented by equations. The substances entering into the reaction are called the factors; those issuing from the reaction are called the products. The symbols and formulas of the factors connected with the sign +, meaning together with, are placed at the left of the equality sign, and those of the products at the right.

Chemical reactions are of three kinds:

1. Two or more elements or compounds unite to form a single product. This is called *combination*, or the reaction is called a *synthetical reaction*. A good illustration of this kind of action is seen in the case, previously mentioned, where magnesium is heated in the air. The magnesium, it will be remembered, burns with the formation of a compound of magnesium and oxygen. The formula of this compound is MgO , and the simplest way to write the equation would be:

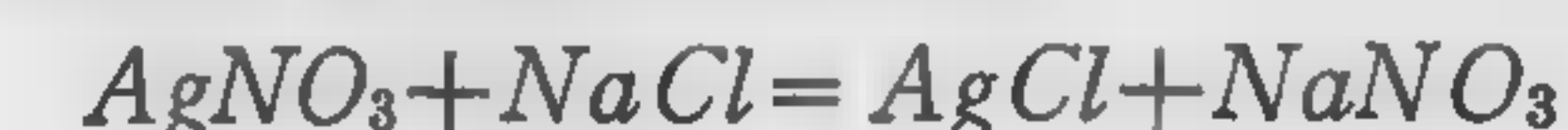


2. A compound breaks up into two or more products. This is called *decomposition*, or the reaction is called an

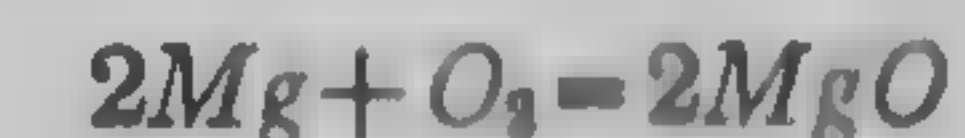
analytical reaction. A good illustration of this kind of reaction is furnished by the experiment previously mentioned in which mercuric oxide is heated, and thus decomposed into mercury and oxygen. The simplest way to write the equation would be:



3. Two or more compounds react on each other with the formation of two or more other compounds, or a compound and an element so react on each other as to result in the production of another compound and element. This kind of reaction is called *double decomposition*, *metathesis*, or *metalepsy*. This kind of reaction may be illustrated by the change occurring when solutions of silver nitrate and common salt (sodium chloride) are mixed. The reaction that takes place may be represented by the equation:

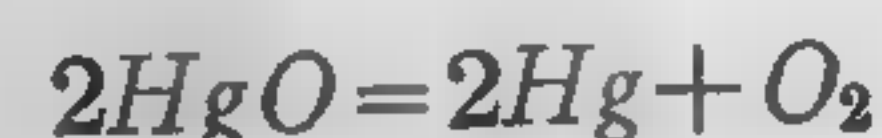


As the chemical change always takes place in the molecules, the equation should be so written as to show the change as it occurs in the molecule. This is done in the third equation, but is not done in the first and second ones. The first equation shows that a molecule of magnesium oxide, MgO , is formed by the union of an atom of magnesium and an atom of oxygen; but there are no free atoms of magnesium and oxygen to start with. These are in the form of molecules, and consequently the equation should be written:

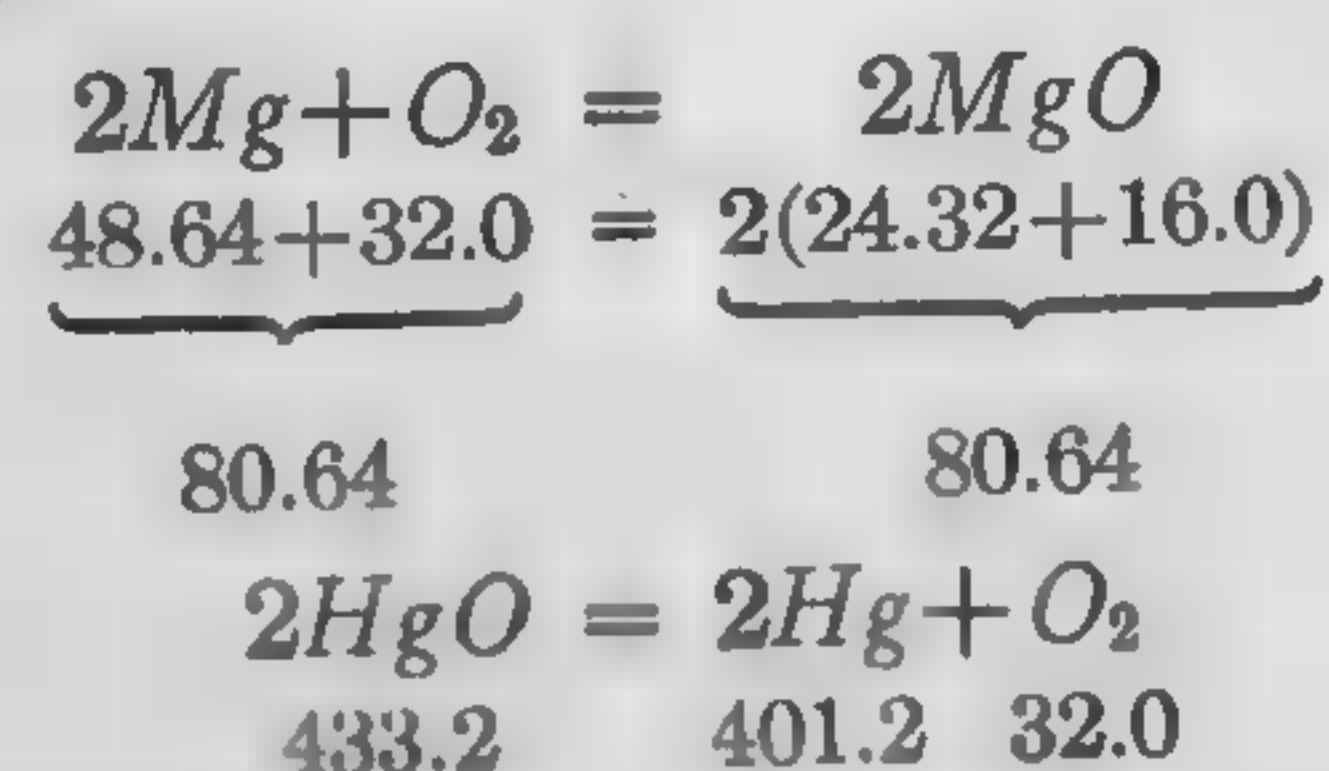


This equation shows that 2 molecules of magnesium and 1 molecule of oxygen, consisting of 2 atoms, unite to form 2 molecules of magnesium oxide. Similarly with the second equation. This would show that a molecule of mercuric oxide yields an atom of mercury and an atom of oxygen upon being decomposed by heat. This is true so far as it goes, but it does not express all that takes place. It is believed that the mercury atoms remain uncombined, and consequently this part of the equation is correct; but the oxygen atom, on account of its great activity, would not remain in the uncombined, or nascent, condition more than an instant, and as there are many

atoms of oxygen being liberated at once, these atoms immediately unite with each other, forming molecules of oxygen. Hence, the equation should be written:



This shows that 2 molecules of mercuric oxide yield 2 atoms of mercury and 1 molecule of oxygen containing 2 atoms. As each atom and molecule has a definite weight, it is evident that these equations not only express the fact of reaction and the relative number of molecules and atoms involved, but that they also indicate the quantities by weight concerned in them. Thus, we may write the equations with the atomic and molecular weights as follows:



Consequently, if we burn any given weight of magnesium, we can calculate the weight of oxygen that will unite with it, and the weight of the magnesium oxide that will be formed. For instance, if we burn 48.64 grams of magnesium, 32 grams of oxygen will be consumed, and, as matter is never created or destroyed, 80.64 grams of magnesium oxide must be formed. If 433.2 grams of mercuric oxide are heated until completely decomposed, the result will be 401.2 grams of mercury and 32 grams of oxygen. If half this weight of mercuric oxide is used, half the given weights of each of the products will be obtained, etc. Thus, it is evident that if the weight of any one of the factors or products of a reaction is known, the weights of all the other factors and products may be calculated from the equation representing the reaction.

23. Facility of Chemical Reaction.—Since a chemical reaction is the result of the reciprocal action of atoms and has for its effect a change in the composition of the molecule, it is evident that it can only take place when these atoms,

and consequently their molecules, are brought into intimate relation, or, more exactly, when the molecules of one of the bodies enter within the sphere of action of other bodies. This sphere is rather limited, as the affinity of the atoms is only exercised at infinitely small distances. In consequence, affinity is often retarded by cohesion, which maintains the relations between molecules of solid bodies. These forces are frequently in opposition, and in order that the first may obtain supremacy it is necessary that the other shall yield. To increase the affinity between two or more bodies it becomes necessary to diminish their cohesion. On this condition, the molecules can enter within the sphere of their reciprocal attraction, and the atoms of one body can attract those of the other.

Experience teaches us that this cohesion can to a certain extent be overcome and chemical reaction facilitated when the acting substances are brought into the liquid or gaseous state. Hence, either heat, by which bodies are vaporized, or solution, by which bodies are liquefied, is an important aid in producing chemical reaction.

24. Effect of Heat on Gases.—The effect of heat on gases was treated in *Physics*, but the subject is of sufficient importance that a few additional words in regard to it will not be out of place at this point, even though some of the facts already mentioned be repeated. The normal temperature of gases is taken as 0°C. , and for each increase of 1° temperature, at ordinary pressure the volume of the gas increases $\frac{1}{273}$ * of its volume at 0° . Hence, Gay-Lussac's law may be stated:

If the pressure remains constant, every increase of 1°C. produces in a given quantity of the gas an expansion of $\frac{1}{273}$ of its volume at 0° .

Thus, if the volume of a gas at 0° is represented by V , its volume V' at t° will be

$$V' = \frac{V(273 + t)}{273}$$

* Probably $\frac{1}{273.15}$ is the most exact value for the expansion, but in all practical chemical work the $\frac{1}{273}$ is dropped and $\frac{1}{273}$ is used.

25. Effect of Pressure on Gases.—This was also treated in *Physics*, but on account of its importance, will be mentioned again here. The normal pressure is taken as 760 millimeters of mercury, and any change in the pressure produces a corresponding change in the volume of the gas, according to Mariotte's law.

The temperature remaining the same, the volume of a given quantity of gas varies inversely as the pressure.

26. Avogadro's Law.—In 1811 the Italian chemist Avogadro enunciated the law that usually bears his name, and by pursuing an entirely independent course of investigation, the French physicist Ampère arrived at the same law in 1814. The law is sometimes spoken of as Ampère's law, though by right of precedence it is generally known as the law of Avogadro.

Equal volumes of all substances, either elemental or compound, in the gaseous state, at the same temperature and pressure, contain an equal number of molecules.

From this law it obviously follows:

1. That the molecules of all gaseous bodies must be of equal size, or at least occupy the same amount of space.
2. That the weight of a molecule of any gas—compared with that of a molecule of hydrogen—is proportional to the weight of any given volume of the gas—also compared with an equal volume of hydrogen.

If, for instance, 1 liter of chlorine weighs 35.18 times as much as 1 liter of hydrogen, 1 molecule of chlorine must weigh 35.18 times as much as 1 molecule of hydrogen, if the above law is true.

This law is incapable of direct absolute proof, but it is in accordance with a large number of well-known facts, and is undoubtedly true if the molecular theory is true, and may therefore be used in helping to determine molecular weights. That it has an important bearing on this subject may be shown as follows:

If 1 volume of hydrogen and 1 volume of chlorine are mixed and the mixture is exposed to the light, 2 volumes of hydrochloric acid is obtained; and if it is assumed that 1 volume of

these gases contains 500 molecules of hydrogen and chlorine, respectively, there will be 1,000 molecules of the compound. By submitting hydrochloric acid to an analysis, it is found that each of its molecules is composed of 1 atom of hydrogen and 1 atom of chlorine; and since the 1,000 molecules of hydrochloric acid were formed from 500 molecules of hydrogen and 500 molecules of chlorine, it is evident that each of these molecules must have furnished 2 atoms.

From this fact it can be stated that a molecule of hydrogen is composed of 2 atoms.

If, then, it is further assumed that the weight of an atom of hydrogen is 1, so as to serve as a unit, the weight of a molecule of hydrogen, that is, its *molecular weight*, will be 2.

27. Density.—Density is the mass of unit volume of a substance. The terms density and specific gravity have practically the same meaning. The **density**, or **specific gravity**, of a substance is the ratio of the weight of a certain volume of the substance to that of an equal volume of some substance taken as a standard. Density is the term generally used in expressing the relative weights of equal volumes of gases when hydrogen is used as the standard. Specific gravity is the term used in connection with solids and liquids when pure water at 4° C. is taken as the standard. The term specific gravity is also sometimes used in connection with gases as compared with air. Thus, for example, the density of nitrogen is 13.93 ($H=1$), which means that a certain volume of nitrogen weighs 13.93 times as much as an equal volume of hydrogen. A volume of copper weighs 8.95 times as much as an equal volume of water, hence, the specific gravity of copper is 8.95. If air is taken as the standard, then a volume of nitrogen will weigh .971 times as much as an equal volume of air, and the specific gravity of nitrogen is .971 ($air=1$). As these terms are used exclusively in these connections it is not necessary to refer to the standard when the values are given. Density in the case of a gas always refers to the hydrogen as a standard, specific gravity of a gas refers to air, and specific gravity of a solid or liquid refers to water, unless the standard is given.

Density and specific gravity bear no relation to atomic weights. It is true that sometimes the density and atomic weight of a gas have the same numerical value, but this is true only in those cases where the molecule of the gas is diatomic.

When hydrogen is used as a standard, the molecular weights of a substance, elemental or compound in the gaseous state, may be found by multiplying its density by 2. Conversely, its density may be obtained by dividing the molecular weight by 2.

The weight of a liter of any substance in a gaseous state is calculated by multiplying its density compared with hydrogen, half of its molecular weight, by the weight of a liter of hydrogen (.089873 gram). Again, the density of a substance may be found by dividing the weight of a liter of the gaseous substance by the weight of a liter of hydrogen.

EXAMPLES FOR PRACTICE

1. What is the molecular weight of: (a) water if the density of water vapor is 9? (b) Of oxygen if its density is 16?
Ans. $\begin{cases} (a) 18 \\ (b) 32 \end{cases}$
2. What is the density of ammonia gas if its molecular weight is 17.034?
Ans. 8.517
3. What is the weight of a liter of oxygen if its density is 16?
Ans. 1.438, nearly

28. Diffusion of Gases.—Every gas has a tendency to mix with another gas when placed in contact with it. This is due to the vibrations of the molecules, and the phenomenon is known as *gaseous diffusion*. This tendency of gases to intermingle can be shown by taking two wide-mouthed bottles, one containing hydrogen and the other oxygen, and placing them mouth to mouth, the bottle containing the hydrogen being placed uppermost. If, after a time, the gas in either bottle is examined it will be found that some of the hydrogen has passed into the bottom bottle containing the oxygen, even though the latter gas is much heavier than the former, and that some of the oxygen has passed into the upper bottle containing the hydrogen. This intermingling of the two gases takes place, even through tubes of considerable length; thus, if the bottles

are connected by means of glass tubes 20 or 30 inches in length, after a time the two gases will be found to have become mixed. This can be proved by applying a lighted taper to the mouth of either bottle, when an explosion will occur.

The diffusion of gases may also be illustrated by means of the apparatus shown in Fig. 1. It consists of a porous cup, or jar, *a*, similar to those

used in galvanic batteries, into the open end of which a tight-fitting, singly perforated stopper is forced; a glass tube *b*, 2 or 3 feet long, is passed through the hole in the stopper. If the connections are not air-tight they are made so by covering the stopper with sealing wax. The apparatus is held in a suitable support *c*, so that the lower end of the tube *b* dips beneath the surface of the water in the pneumatic trough *d*. Now, if a bell jar *e* containing dry hydrogen is placed over the porous jar so that it is surrounded by



FIG. 1

hydrogen, the air will pass out through the glass tube and bubble up through the water in the pneumatic trough. When the bubbles cease, if the bell jar is removed, the water will rapidly rise in the tube for a time, and then gradually sink to the level of the water in the trough. These phenomena are caused by the diffusion of the gases. The porous jar is filled with air, and, when the bell jar is brought over it, is surrounded by hydrogen. The hydrogen, being so much lighter than the air, diffuses

through the walls of the jar much more rapidly than the air passes out, thus causing pressure in the jar, which is relieved by air being forced down through the tube and bubbling up through the water. When equilibrium is restored, the atmosphere in the jar is principally hydrogen, and when the bell jar is removed the jar is surrounded by air. The hydrogen immediately begins to pass out faster than the air can pass in, and a partial vacuum is thus formed, which causes the water to rise in the tube. This is known as Graham's experiment, and by using different apparatus, with which careful measurements could be made, and experimenting with various gases, he arrived at the law that bears his name, viz.:

The rate of diffusion of gases is inversely as the square root of their densities.

According to this law, if hydrogen and oxygen are mixed, as their densities are approximately 1 and 16, respectively, the hydrogen would diffuse about four times as rapidly as the oxygen. Some phenomena have been observed that tend to show that this law does not hold good in all cases, but not sufficient work has been done that a final decision can be reached at the present time. It is known that if a light gas like hydrogen and a heavy one like carbon dioxide are led into a receptacle, much of the heavy gas will pass directly to the bottom and the light gas will largely rise to the top; but it is believed that if left together a sufficient time, they will diffuse so that the vessel will contain a homogeneous mixture of the two gases.

29. Valence.—All elements have a chemical attraction for one another and have the power of holding other atoms in combination. This power of holding other atoms in combination varies with the different elements. For example, sulphur unites with hydrogen and forms the compound H_2S ; carbon and hydrogen combine and form CH_4 . Hence, carbon requires 4 atoms of hydrogen and sulphur requires but 2 atoms of hydrogen. Again, oxygen requires 2 atoms of hydrogen to form H_2O ; nitrogen forms NH_3 with 3 atoms of hydrogen; and chlorine combines with 1 atom of hydrogen to form HCl . Since one element cannot combine partly with another element

and have an unsatisfied attraction, each attraction must be completely satisfied before combination can occur. The preceding examples demonstrate the fact that there is a quantitative attraction between atoms, or, in other words, the number of atoms of one element that will combine with the atoms of another element to form a chemical compound is a definite one. This capacity of one atom for another is known as the **valence** of that element. Therefore, the valence of an element may be defined as *the combining power possessed by an atom*.

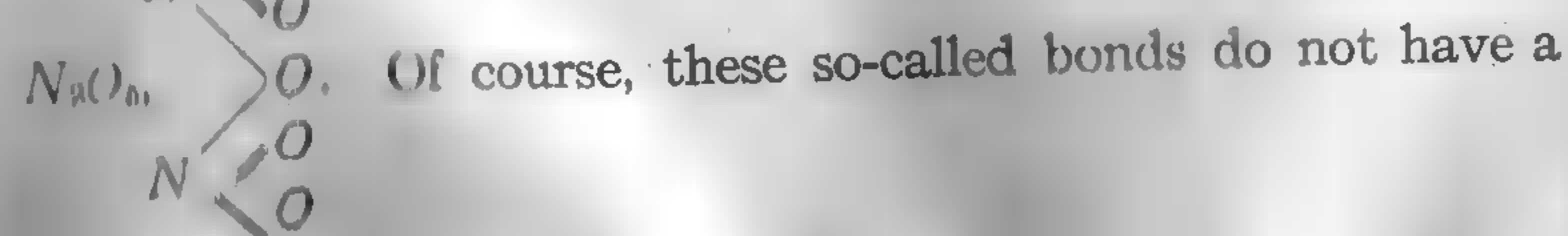
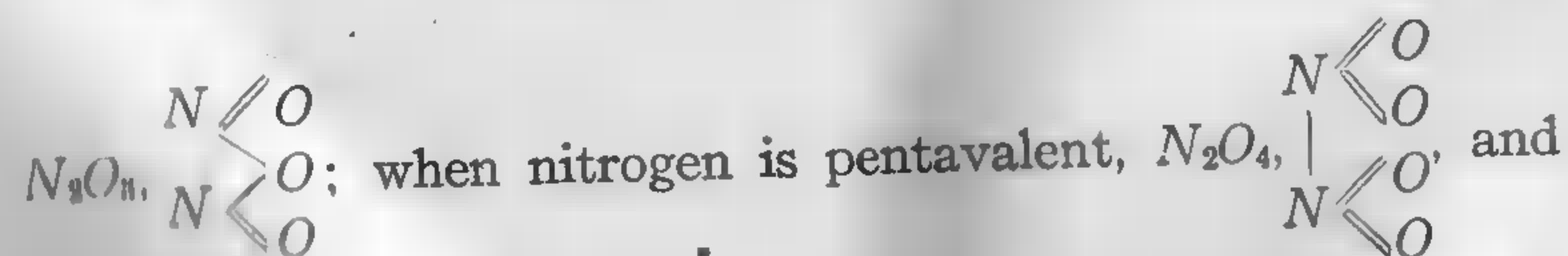
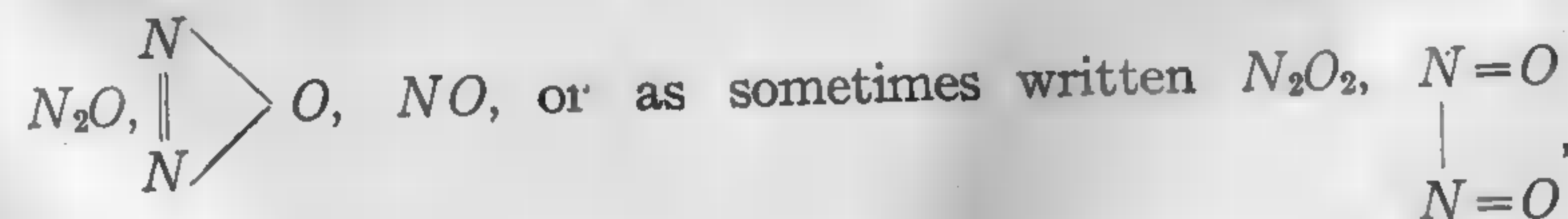
Hydrogen is taken as the unit of valency, as it belongs to the class of elements having the lowest combining power. Hence, chlorine, which requires 1 atom of hydrogen, is said to have a valence of 1, or to be *univalent*; sulphur and oxygen, which require 2 atoms of hydrogen, are said to have a valence of 2, or to be *bivalent*; nitrogen unites with 3 atoms of hydrogen and has a valence of 3, or is *trivalent*; carbon requires 4 atoms of hydrogen for combination; hence, it has a valence of 4, or is said to be *quadrivalent*. Most of the elements fall into one of these classes, although some have the power of uniting with five, six, and even seven univalent atoms. These elements are said to have a valence of 5, 6, and 7, and are called *pentavalent*, *sexivalent*, and *septivalent*, respectively.

The valencies of the elements have been accurately determined. It has been found, however, that some atoms have the power of attracting other atoms in different degrees of strength, or, in other words, have varying valencies. For example, nitrogen unites with oxygen to form N_2O , NO , and N_2O_3 , in which the nitrogen is trivalent, and N_2O_4 and N_2O_5 , in which it is pentavalent. The principal causes of variation seem to be temperature, and the character of the element with which the given element combines. The effect of temperature may be illustrated by means of the compounds of phosphorus and chlorine. When these elements unite at ordinary temperature they form the compound PCl_5 , but if this is heated it gives off chlorine and becomes PCl_3 . Thus, it is seen that at ordinary temperatures phosphorus appears to be pentavalent, but at higher temperatures it appears to be trivalent. It is found to be a general rule that the higher the temperature the lower the

valence. The variation in valence of an element as dependent on the character of the element with which it combines may be illustrated by means of sulphur, which was given previously as an example of a bivalent element. Sulphur can be made to unite with but 2 atoms of hydrogen to form H_2S , showing that in combination with this element it is bivalent, and only bivalent, but it unites with 6 atoms of fluorine, forming SF_6 , thus indicating that it is sexivalent toward fluorine. With oxygen, sulphur forms two compounds, SO_2 and SO_3 . As oxygen is bivalent, it would appear from the compound SO_2 that sulphur is quadrivalent, and from SO_3 that it is sexivalent toward oxygen.

It is customary to speak of valence as bonds of affinity, or merely bonds, and these are represented graphically by means of dashes—one dash to represent each bond. Thus, as hydrogen and chlorine each belong to the class having the lowest valence, they are each said to have one bond and are written $H-$ and $Cl-$. Hydrochloric acid, the compound formed when these elements unite, is written $H-Cl$, showing that the bond of one has united with the bond of the other. The elements having higher valence are written with the appropriate number of bonds; thus, $-S-$ or $S<$, $-N<$, $-C-$.

In the case of the compounds of nitrogen and oxygen, these would be represented as follows: when nitrogen is trivalent,



VALENCE OF ATOMS

Monads:

Hydrogen
Lithium
Rubidium
Cæsium
Potassium
Sodium
Silver
Fluorine, I, III
Thallium, I, III
Chlorine, I, III, IV, V, VII
Bromine, I, III, V, VII
Iodine, I, III, V, VII

Triads:

Boron
Aluminum
Gallium
Indium
Yttrium
Scandium
Ytterbium
Cerium, III, IV
Lanthanum
Erbium
Gold, I, III
Antimony, III, V
Bismuth, III, V
Nitrogen, I, III, V
Phosphorus, III, V
Arsenic, III, V
Samarium
Terbium

Pentads:

Columbium
Tantalum
Vanadium, II, III, V

Dyads:

Oxygen
Magnesium
Zinc
Cadmium
Beryllium
Mercury, I, II
Copper, I, II
Calcium
Strontium
Barium
Cobalt, II, III
Nickel, II, III
Sulphur, II, IV, VI
Selenium, II, IV, VI
Tellurium, II, IV, VI
Manganese, II, III, IV, VI, VII

Tetrads:

Germanium, II, IV
Silicon
Thorium
Zirconium
Carbon
Titanium, III, IV
Tin, II, IV
Platinum, II, IV
Palladium, II, IV
Lead, II, IV
Iron, II, III, VI
Chromium, II, III, VI

Hexads:

Tungsten, II, IV, VI
Molybdenum, II, III, IV, VI
Ruthenium, II, IV, VI, VIII
Rhodium, II, III, IV
Iridium, II, III, IV
Osmium, II, III, IV, VIII
Uranium, II, IV, VI

material existence; they are used only as a convenient method of expressing the fact that 1 atom has the power of holding in combination a certain number of other atoms. It is a *graphic* method of expressing the facts of valence.

According as their valence is 1, 2, 3, 4, 5, 6, or 7, atoms are called *monads*, *dyads*, *triads*, *tetrads*, *pentads*, *hexads*, or *heptads*, which names are derived from the Greek numerals.

The valences of the different elements are shown in the accompanying list. Each element that possesses more than one valence is placed under that heading which signifies the most frequently occurring valence of that element.

30. Graphic Formulas.—It is now known almost certainly how the atoms are combined in many compounds, and to show the valence, and how they are united, graphic formulas are used. These are formulas that represent all that is known in regard to the constitution of the molecules represented. Thus, the graphic formula for hydrochloric acid would be $H-Cl$, showing that the univalent atoms of hydrogen and chlorine are combined, the bond of each being mutually satisfied. The graphic formula for water, $H-O-H$, shows that the bivalent atom of oxygen is combined with the 2 univalent atoms of hydrogen, the bond of each of the atoms of hydrogen satisfying one of the bonds of the oxygen, so that all the bonds are mutually satisfied. The graphic formula for sulphuric acid, $\begin{array}{c} H-O \\ H-O \end{array} > S < \begin{array}{c} O \\ O \end{array}$, shows that one bond of each

of 2 atoms of oxygen is united to an atom of hydrogen, while the other bond of each of these 2 atoms is united to the sexivalent atom of sulphur, the other four bonds of it being satisfied by 2 bivalent oxygen atoms.

That the molecules are formed as represented is not capable of direct proof, but after carefully considering the evidence, probably no one will doubt that the compounds are formed exactly as represented by the formulas.

31. Metals and Non-Metals.—The elements are ordinarily classified as metals and non-metals, but this classifi-

cation is by no means perfect, for there is no sharp line of demarcation between the two groups, the properties gradually varying from the extremely electropositive to the extremely electronegative. Another reason for confusion lies in the fact that there is no strict definition for a metal. The classification depends on both chemical and physical properties, and consequently a chemist would ordinarily classify an element like antimony, nearly all of whose chemical properties are non-metallic, as a non-metal; while a physicist would probably classify it as a metal, for its physical properties are nearly all metallic. Physically, metals ordinarily have a peculiar luster known as metallic luster, which may be seen in the case of polished silver or steel, or freshly cut lead; and are comparatively good conductors of heat and electricity. The non-metals do not possess these properties, or if they possess them at all, it is in a less degree. The metals are electropositive, and the non-metals electronegative. Chemically, the metals possess the power of replacing the hydrogen in acids, and their oxides and hydroxides are basic in character. They may therefore be called base-forming elements.

The non-metals do not possess the power of replacing hydrogen in acids, and their oxides and hydrates are of an acid-forming nature. (The terms acid and base will be fully explained in due time.) Such elements as silver, lead, and iron are clearly metals, and chlorine and sulphur are clearly non-metals; but such elements as arsenic and antimony are difficult to classify. As both physical and chemical properties apparently overlap in a number of cases, it seems best to lay less stress on this division and to divide the elements into natural groups based on chemical analogy. It appears that the properties of the metals are, broadly speaking, functions of their atomic weights, and by arranging them according to their atomic weights, they fall into groups having similar properties. This system, known as the *periodic system*, described in *Inorganic Chemistry*, Part 3, forms the basis of the classification adopted in these Sections. To carry out this system strictly would require the treatment of the elements of Family 1 first, but as this would require the treatment of substances with which the student is unfamiliar,

and of processes that would be entirely unintelligible to him at present, it is deemed best to vary the order of treatment somewhat. There are two elements that occur in nature in large quantities, are widely distributed, and may be easily obtained. Their behavior will throw much light on chemical reactions in general, and will give the student an insight into the methods of chemical work. The two elements referred to are hydrogen and oxygen. In the case of hydrogen this will not interfere with the system adopted, for hydrogen seems to be an element standing by itself and has no place in the system except, possibly, as a type.

WEIGHTS AND MEASURES

32. Metric System.—The metric system of weights and measures is almost universally used by chemists. The unit of length is the meter, which is about 39.37 inches. Multiples of this unit are designated by prefixing the Greek words deka (10), hekto (100), and kilo (1,000); hence, 10 meters are known as 1 dekameter, 100 meters as 1 hektometer, and 1,000 meters as 1 kilometer. Subdivisions of the meter are obtained by prefixing the Latin words deci ($\frac{1}{10}$), centi ($\frac{1}{100}$), and milli ($\frac{1}{1000}$); hence, $\frac{1}{10}$ meter is 1 decimeter, $\frac{1}{100}$ of a meter equals 1 centimeter, and $\frac{1}{1000}$ of a meter is 1 millimeter.

The unit of volume is the liter. It is 1 cubic decimeter of volume. The decimal subdivisions and multiples are designated by the same prefixes as in the case of the meter. The unit of weight is the gram. It is the weight of 1 cubic centimeter of water at 4° C. Its decimal multiples and subdivisions are designated by the same prefixes as in the case of the meter. As there are 1,000 cubic centimeters in a liter, a liter of water at 4° C. weighs 1,000 grams. If this simple relation between meter, liter, and gram is thoroughly mastered at the outset, the metric system will present no further difficulties. This relation between the different units, and the fact of its being a decimal system, render it far superior to the complicated English system, for the use of chemists at any rate, and probably for all purposes.

MEASURES OF LENGTH

10 millimeters (mm.)	= 1 centimeter	cm.
10 centimeters	= 1 decimeter	dm.
10 decimeters	= 1 meter	m.
10 meters	= 1 dekameter	Dm.
10 dekameters	= 1 hektometer	Hm.
10 hektometers	= 1 kilometer	Km.

MEASURES OF SURFACE (NOT LAND)

100 square millimeters (mm ² .)	= 1 square centimeter	cm ² .
100 square centimeters	= 1 square decimeter	dm ² .
100 square decimeters	= 1 square meter	m ² .

MEASURES OF VOLUME

1,000 cubic millimeters (mm ³ .)	= 1 cubic centimeter	cm ³ .
1,000 cubic centimeters	= 1 cubic decimeter	dm ³ .
1,000 cubic decimeters	= 1 cubic meter	m ³ .

MEASURES OF CAPACITY

10 milliliters (ml.)	= 1 centiliter	cl.
10 centiliters	= 1 deciliter	dl.
10 deciliters	= 1 liter	l.
10 liters	= 1 dekaliter	Dl.
10 dekaliters	= 1 hektoliter	Hl.
10 hektoliters	= 1 kiloliter	Kl.

NOTE.—The liter is equal to the volume occupied by 1 cubic decimeter of pure distilled water at its temperature of maximum density, or 4° C.

MEASURES OF WEIGHT

10 milligrams (mg.)	= 1 centigram	cg.
10 centigrams	= 1 decigram	dg.
10 decigrams	= 1 gram	g.
10 grams	= 1 dekagram	Dg.
10 dekagrams	= 1 hektogram	Hg.
10 hektograms	= 1 kilogram	Kg.
1,000 kilograms	= 1 ton	T.

NOTE.—The gram is the weight of 1 cubic centimeter of pure distilled water at a temperature of 4° C.; the kilogram is the weight of 1 liter of water; the ton is the weight of 1 cubic meter of water.

Chemists rarely use the expressions dekameter, hektometer, dekaliter, hektoliter, dekagram, or hektogram, preferring to say so many meters, liters, or grams. However, any weight or measure in excess of 10 hektograms, 10 hektometers, or 10 hektoliters is always spoken of as so many kilograms, kilometers, or kiloliters.

33. English System.—Chemists have little if any use for the English weights and measures in actual work, but as this system is in common use in this country, it is sometimes necessary to change results from one system to the other. For this reason it will not be out of place to review the relations of some of the most commonly used units.

One United States gallon has a volume of 231 cubic inches, and contains 4 quarts, or 8 pints. The English imperial gallon contains 277.274 cubic inches; hence, the English gallon is equivalent to 1.20032 United States gallons.

A gallon of pure water at 62° F. (16 $\frac{2}{3}$ ° C.) weighs 133.37 ounces, or 58,350 grains; hence, a pint of pure water at 16 $\frac{2}{3}$ ° C. weighs 16 $\frac{2}{3}$ ounces, or a little over 1 pound, whence the saying "a pint is a pound," although, of course, a pint of any liquid having a specific gravity differing from that of water would have a different weight. The measure termed a *fluid ounce* is a measure of volume, and not of weight, and is equal to $\frac{1}{16}$ part of a pint. In other words, it is approximately the volume of 1 ounce of pure water.

The fluid ounce bears the same relation to the avoirdupois ounce as does the cubic centimeter to the gram. When directions are given to dissolve 1 part by weight of a solid in 10 parts (or any other number of parts) by weight of water, either ounces in fluid ounces or grams in cubic centimeters may be taken.

One fluid ounce is equivalent to 29.57 cubic centimeters, and contains 455.86 grains of water at 16 $\frac{2}{3}$ ° C. One gram is equivalent to 15.43236 grains, and 1 avoirdupois ounce is equivalent to 28.3495 grams. The most exact figures obtainable are given here, but in practice it is seldom necessary to carry the values farther than the second place of decimals.

As it is the general custom to use the centigrade thermometer in all chemical calculations and investigations, the temperatures given in this and the following Sections will always be in degrees centigrade, unless otherwise stated.

It should be borne in mind that the absolute temperature of a body is its temperature in degrees C. + 273 $\frac{1}{2}$ °, but in all practical work the fraction is dropped and 273° is used.

The following list gives some of the most common multiples for the conversion of the English system into the metric:

Centimeters $\times .3937$ = inches.

Cubic centimeters $\times .0338$ = fluid ounces.

Gallons $\times 3.785$ = liters.

Grains $\times .0648$ = grams.

Gram = 15.432 grains.

Inches $\times .0254$ = meters.

Liter = 1.0567 quarts, liquid.

Ounces, Troy $\times 1.097$ = ounces, avoirdupois.

Ounces, avoirdupois $\times .9115$ = ounces, Troy.

Ounce, avoirdupois = 28.35 grams.

Ounce, Troy = 31.104 grams.

Quart, liquid = .94636 liter.

THE BALANCE

34. As a full knowledge of how to manipulate the balance is of such vast importance to chemists, a full description will not be out of place at this point.

A most useful form of balance, having a weighing capacity of from 1 milligram to 200 grams, is shown in Fig. 2. The balance is enclosed in a glass case with sliding doors, and rests on a solid wooden box *A A*, in which is a drawer that may be used for weights, etc. A metallic pillar *B* is screwed to the top of the box, and supports, in a cradle *C* at the top, the central knife edges of the beam *D*. On the ends of the beam, at *E*, are also fitted knife edges, on which hang the hooks *F*, and from these are suspended the bows *G* that carry the pans *H*. In the center of the front of the base of the balance is fixed a handle, or knob, *I*. In the position shown in the figure, the pans are at rest on the balance base. But, on turning this knob to the right, the whole of the balance is raised by means of an eccentric that actuates a sliding rod within the pillar *B* and raises the cradle *C*. The pans are then free to swing, and their motion is shown by the index *K*, which is fastened to the center of the beam. The end of this index moves in front of a graduated scale that has a zero mark in the

center. Before using the balance, see that it is level and that the index is exactly in front of the zero mark. On raising the pans by turning the handle *I*, the index should vibrate an equal number of degrees each side of the zero. Should it not do so, one of the pans is slightly heavier than the other, probably through not being quite clean; if so, turn the handle back and set the balance to rest and then dust the whole instrument very carefully, and test again. If still out, the balance may require adjusting, which is done by means of a screw at the end of the

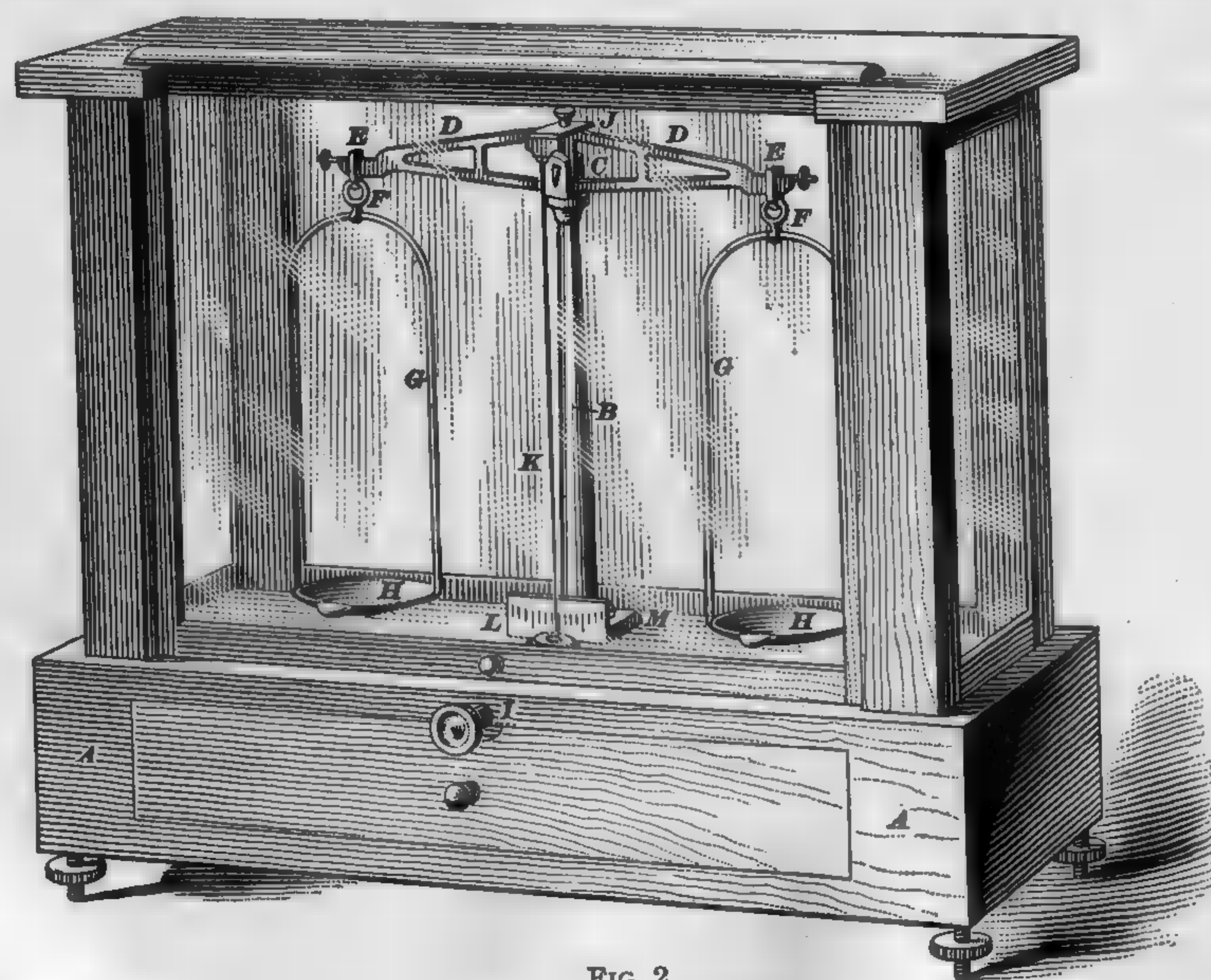


FIG. 2

beam. If the left-hand pan appears to be too heavy, the screw must be screwed outwards from the center of the beam, and in the opposite direction if the right-hand pan is too heavy. However, do not be too quick in adjusting; try repeatedly to get the scales to balance before touching the adjustment screw; many a good balance has been spoiled and accurate weighing has been made impossible by too frequent adjustment.

Every chemist should keep his balance and weights sacred, and should treat them with the greatest care and consideration.

The weights are usually kept in a box, as shown in Fig. 3. The larger weights are generally made of brass; the smaller ones are made of aluminum or platinum; each small weight rests in a separate compartment under a glass lid *a b*. For the purpose of lifting the weights, a forceps is used, which has its place in the box.

Accurate weights must under no consideration be touched with the fingers, but always lifted with the forceps.

The arrangement of the weights varies with different makes.

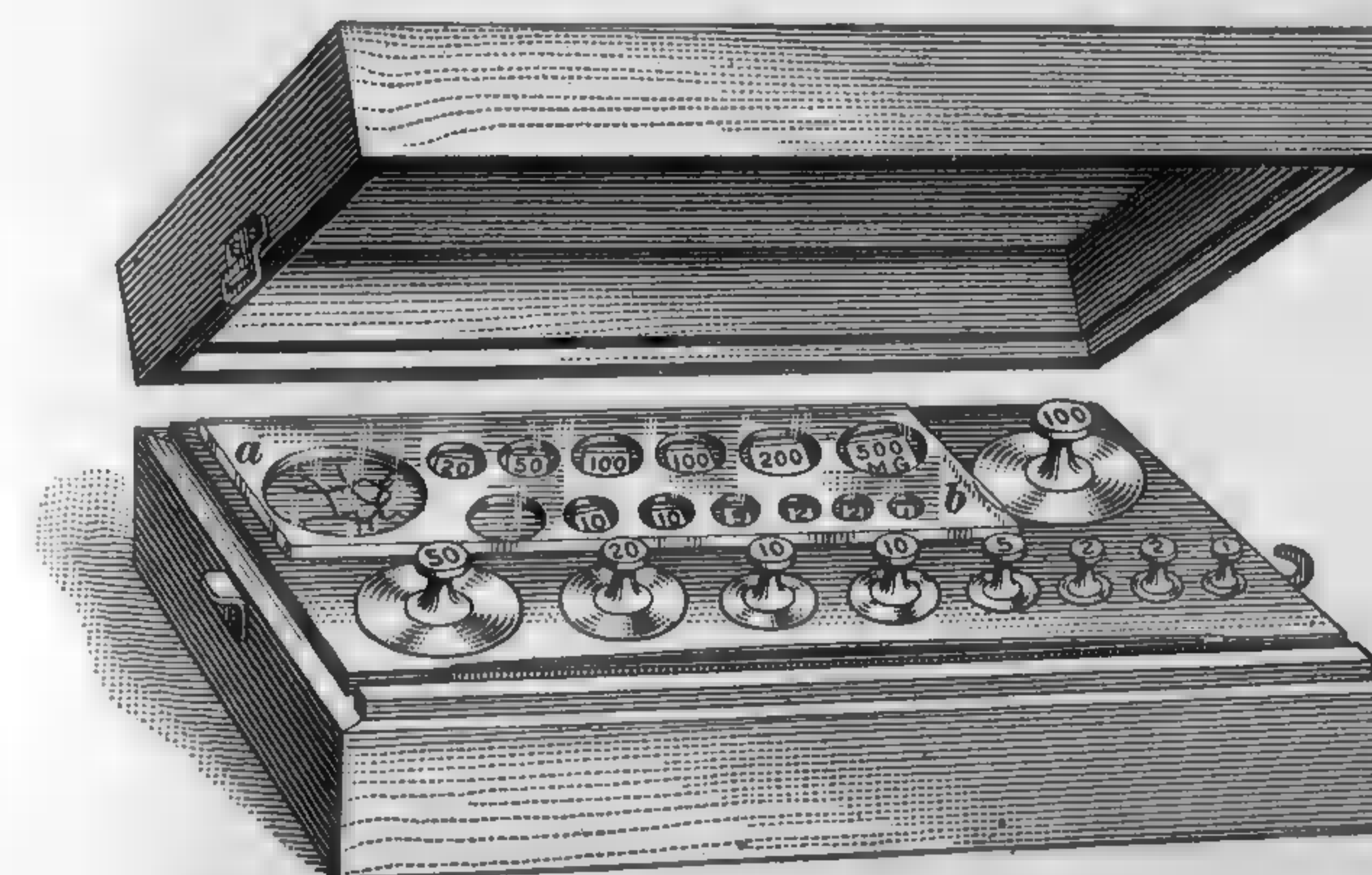


FIG. 3

Fig. 3 shows the usual and most convenient arrangement for a set of weights of from 100 grams to .0001 gram.

Before attempting to weigh, the student must learn not only the denomination of each weight, but also its place in the box. He must be quite as well able to read the weights he has placed in the balance pan from the empty space in the box as from the weights themselves.

35. Method of Weighing. Let us suppose that it becomes necessary to weigh a glass flask. This, in the first place, must be thoroughly cleaned and dried, then placed on the left-hand pan of the balance. Let us assume the weight of the flask to be 138.847 grams, and let us see how these figures are obtained. First, with the balance at rest, place the apparatus in position. Then take the 200-gram weight

from the box by means of the forceps and place it on the right-hand pan; lift the balance by turning the knob *I* to the right, and notice which pan is heavier; lower the balance by returning the knob. In this case the weight will be too heavy, and the index will swing to the left. Put on the 100-gram weight in the pan and lift the balance—the weight is too light and the index will swing to the right. Do not forget that every time a weight (even the smallest) is added or removed, the balance must be set to the position of rest; that is, lowered by turning the handle to the left, and that this must be done very gently and carefully, to prevent dulling or nicking of the knife edges. Now add the 50 gram—too much; remove the 50 and try the 20—not enough; add another 20—too much; remove the 20 and add 10—not enough; add 5—not enough; add 2—not enough; add another 2—too much; remove the 2 and add 1—not enough. As the weights get nearer and nearer to the weight of the flask the beam begins to swing more and more slowly. Having now got to a point at which another gram more than turns the scale, commence in the same way with the fractions of a gram. Try first .5 gram—not enough; add .2—not enough; add another .2—too much; remove the .2 and try .1—not enough. As at this stage the beam swings very slowly, it is advisable to start it by wafting a current of air down on one of the pans with the hand, until the index swings very nearly to the extremity of the scale. Try next the .05-gram weight; the index swings perhaps just 6 divisions to the left and 5 to the right—the weight is too much; remove the .05 and try .02—not enough; add another .02—not enough. Next add .005—not enough; but more likely than not the index swings only a fraction of a degree farther to the right than to the left. Add .002—the index swings the same number of degrees each side of zero. The weights now exactly balance the flask. Now we must read the weights; this must first be done from the box, reading the empty spaces. In this case we have $100 + 20 + 10 + 5 + 2 + 1 = 138$. Against the words "Weight of the flask" write this number in your notebook. Next read off the decigram-weight spaces; there are empty $.5 + .2 + .1 = .8$. Write 8 after 138. The centigrams come next; there are $.02 + .02 = .04$. Write 4 after 138.8. The milligrams are

read in the same manner, and are $.005 + .002 = .007$. Write 7 after 138.84. The whole figure will then read, "Weight of flask = 138.847 grams."

Having thus read the weight from the empty spaces in the box, next take out the weights and check off your reading as the weights are returned to their proper places. This double reading greatly reduces the chances of error in recording the weight of a substance. These operations have been described in full, because they are the foundations of exact chemical work; but they are much shorter in practice than they appear on paper, and the student should in no way become discouraged.

Remember in every case to use the greatest care when working with a balance; never touch scales or weights with the fingers, nor leave them about out of their proper place in the box; on the contrary, take every precaution to see that they are not soiled, exposed to acid fumes, or otherwise injured.

GLASS

36. Glass is indispensable to the chemist on account of its transparency, the ease with which it can be worked in any shape when hot and plastic, and its not being attacked appreciably by most chemicals. Its disadvantage is its brittleness. It is particularly liable to break on heating; being a bad conductor of heat, one part of the glass expands on being heated before the neighboring parts become warm.

When boiling water or any other liquid in a glass vessel, always use a tripod and put a piece of wire gauze between the vessel and the flame. The gauze distributes the heat over the bottom of the vessel, and the liquid can be heated until it boils without accident; that is, without cracking the glass. Or, place some fine sand in an iron tray; put the tray on the tripod stand and place the glass vessel on the sand. The heat is distributed by the sand, and the glass vessel can be heated safely. The tray containing the sand is known in the laboratory as a *sand bath*.

37. To Cut Glass Tubing.—It will generally be possible for the student to fit up the apparatus required for his experi-

ments, and he will frequently have to cut a piece of glass tubing to a desired length. This is done very easily. Take a sharp file and make a nick in the glass tube; then hold the

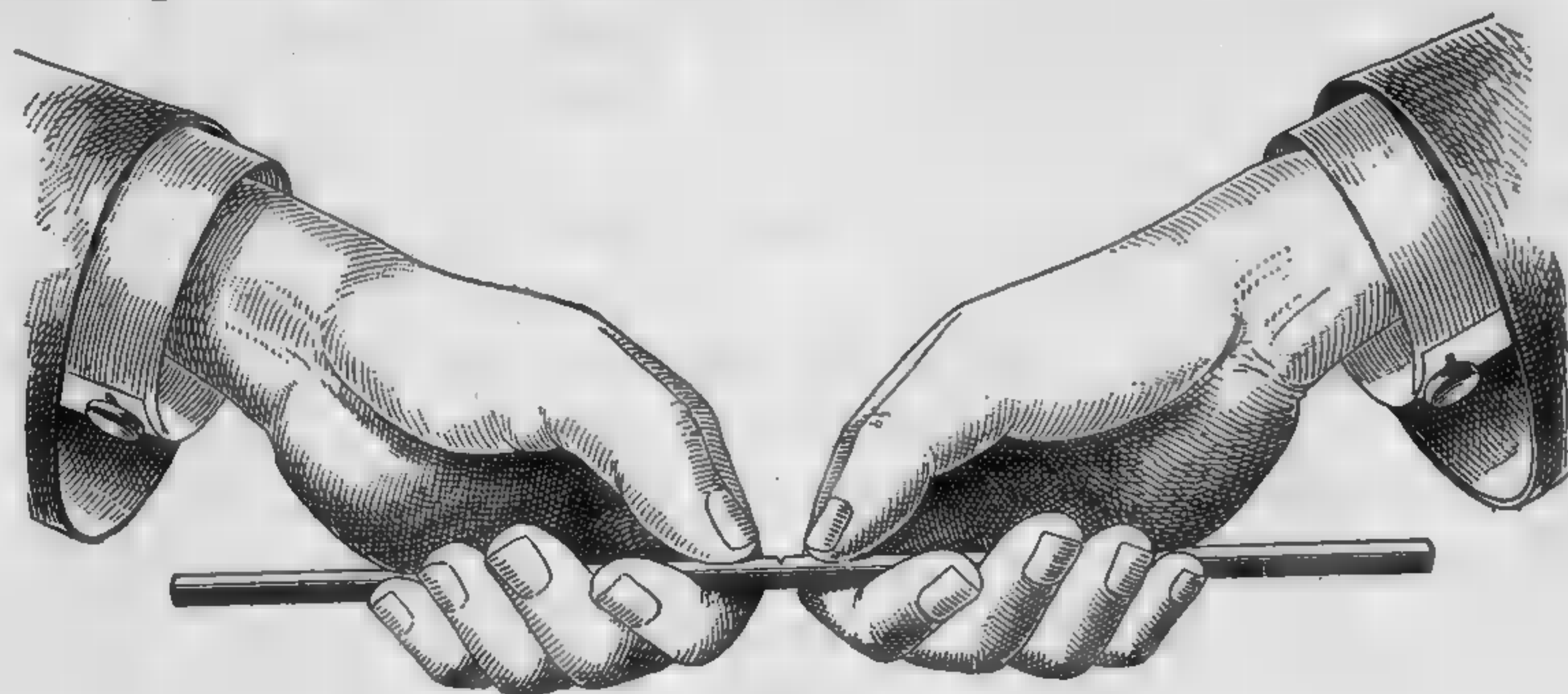


FIG. 4

tube in both hands; the two forefingers should be together immediately under the nick, the two thumbs above. Turn the wrists outwards and downwards, round the forefingers as axes, at the same time pulling the hands apart (see Fig. 4).

38. To Bend and Draw Glass Tubing.—Take one end of the piece of tubing to be bent in each hand and hold it



FIG. 5

lengthwise in a flat gas flame (fishtail or batwing, not the Bunsen flame), as shown in Fig. 5. Keep the glass slowly moving around in the flame until it softens, taking care not

to move it more by one end than by the other. As soon as it softens sufficiently, raise the ends (Fig. 6) until a bend of the desired angle is obtained. To draw a jet on a glass tube, heat in a hot flame, with constant turning of the tube, until the glass becomes soft. Continue revolving the tube and remove it from the flame, hold in a vertical position and draw apart with a steady pull. When cold, cut off with a file at the desired point.

39. To Round the Ends of Glass Tubing.—The sharp edges left at the ends of glass tubing when it is cut must be carefully rounded; otherwise, the tubes will not slide easily through stoppers, and are apt to cut any rubber tubes that



FIG. 6

are slipped over them. The rounding is best accomplished by holding the end in the hot part of a Bunsen flame until it softens, when it will become smooth and round. It must not be held in the flame too long or the opening of the tube will tend to close. If the glass tube is moistened before slipping it through a stopper or slipping a piece of rubber tubing over it, it will be found that these operations are much more easily accomplished than with a dry tube. Wetting the stopper or rubber tubing, of course, amounts to the same thing.

After glass tubing has been heated it appears to be more brittle than at first. This brittleness can be overcome by allowing it to stand several hours before using.

PHYSICAL PROCESSES USED IN CHEMISTRY

40. Separation.—The chemist frequently finds, in the course of experiments, that it is necessary to separate bodies from one another; the processes employed for this purpose are varied, depending on the nature of the substances. As in many future operations it will be necessary to use one or more of them, it is advisable that at this stage they should be studied. As a rule, one of the elements or compounds in a mixture possesses some particular property that the other does not; thus, one may be soluble in water and the other insoluble, which at once affords a means of separating them. The principal methods of separation employed are *solution*, *decantation*, *evaporation*, *filtration*, *crystallization*, *distillation*, *sublimation*, and *ignition*.

41. Solution, Decantation, and Evaporation.—A mixture of two bodies, only one of which is soluble in water, is separated by the action of that solvent.

Solution is the disappearance of a substance in a given liquid. The substance is said to be *dissolved* in the liquid, the liquid is called the *solvent* of the substance, and the combined mass of liquid and substance is said to be a *solution* of the substance. The dissolved substance loses its original physical properties. Weakening the cohesion of the molecules of a substance by reduction to a fine powder or by heat hastens the solution.

EXPERIMENT 1.—Take some mixture of sand and salt, place in a test tube, add water, and shake up; allow the sand to subside; the clear solution on the top is to be carefully poured off, without disturbing the sediment, into a porcelain basin (evaporating basin). The process is known as *decantation*.

Place a piece of wire gauze on one of the rings of the retort stand, adjusted at a suitable height above the Bunsen burner; put the evaporating basin containing the solution of salt on the gauze and light the

burner, keeping the flame small; the water will gradually evaporate and crystals of salt will form. The water has been driven off by *evaporation*. (The object of placing the wire gauze under the basin is to prevent the flame coming in actual contact with and cracking it.)

In cases where both bodies are insoluble in water, some substance has to be selected that acts on the one and not on the other.

EXPERIMENT 2.—Place some of a mixture of sand and finely powdered marble in a test tube, add some distilled water, and heat. Take out a few drops of the water and evaporate them on a piece of clean platinum foil; they entirely disappear, or only leave the very slightest stain on the foil. This is the usual test employed to ascertain whether a solvent has dissolved anything or not. Decant off the water and add dilute hydrochloric acid to the mixture; effervescence occurs. When this is over, again take out a few drops of the liquid and evaporate on the foil; a considerable residue will remain. The best way to get a few drops out of a test tube is to put in the end of a glass tube; then close the top with the finger and withdraw it. On removing the finger the small portion it contains runs out.

The separation in this experiment depends on the fact that marble is dissolved by hydrochloric acid, while sand is not affected by it.

42. Filtration.—Cases frequently occur in which decantation is not advisable or practicable for the purpose of separating a liquid and a solid; the solid, for instance, may be so finely

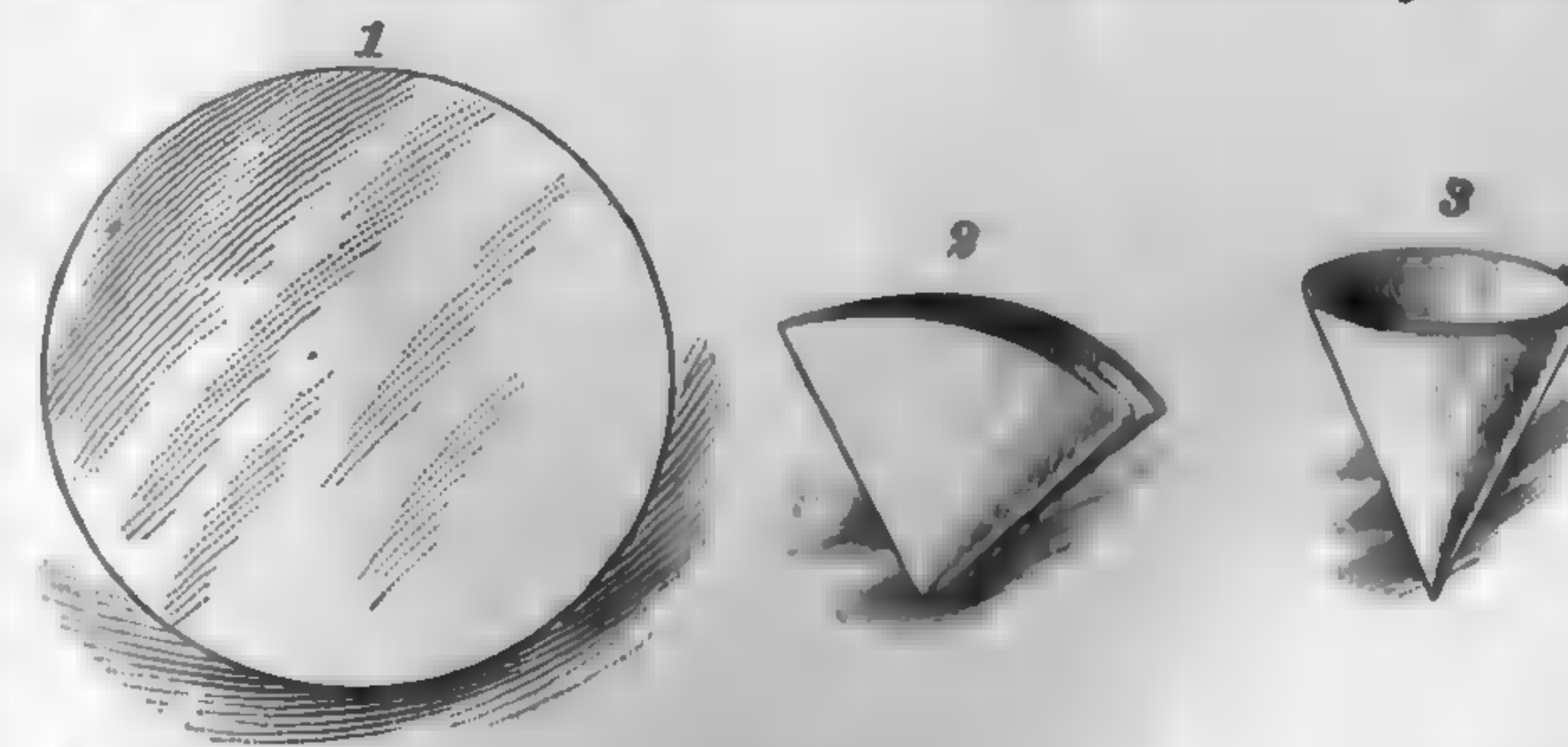


FIG. 7

divided that it floats in the liquid, or remains suspended, giving the liquid a muddy appearance. Under such circumstances the chemist must resort to *filtration*.

EXPERIMENT.—Take a piece of filter paper (soft blotting paper will do, if you have not the especially prepared filter paper at hand) about $3\frac{1}{2}$ inches in diameter, and double it twice; then open it into a cone, taking three folds of paper on the one side and one on the other, as shown in Fig. 7.

Place this cone of paper in a glass funnel, which it will just fit, and moisten it with water. Care must be taken that the point of the folded filter does not get broken. Then mix a solution of barium chloride with some sodium carbonate; a white precipitate will result. Pour the whole on the filter, holding a glass rod or thin piece of glass tubing against the lip of the beaker, or test tube, down which the liquid runs (see Fig. 8); the clear liquid, known as the *filtrate*, passes through, and is collected in a bottle or beaker; the precipitate, which consists of barium carbonate, remains on the filter. Pour some clean water on it for the purpose of washing. After this has drained off, remove the beaker, punch a hole through the bottom of the filter, wash the precipitate into an evaporating basin and dry it. The

filtrate contains sodium chloride (common salt), which may be obtained by evaporation.

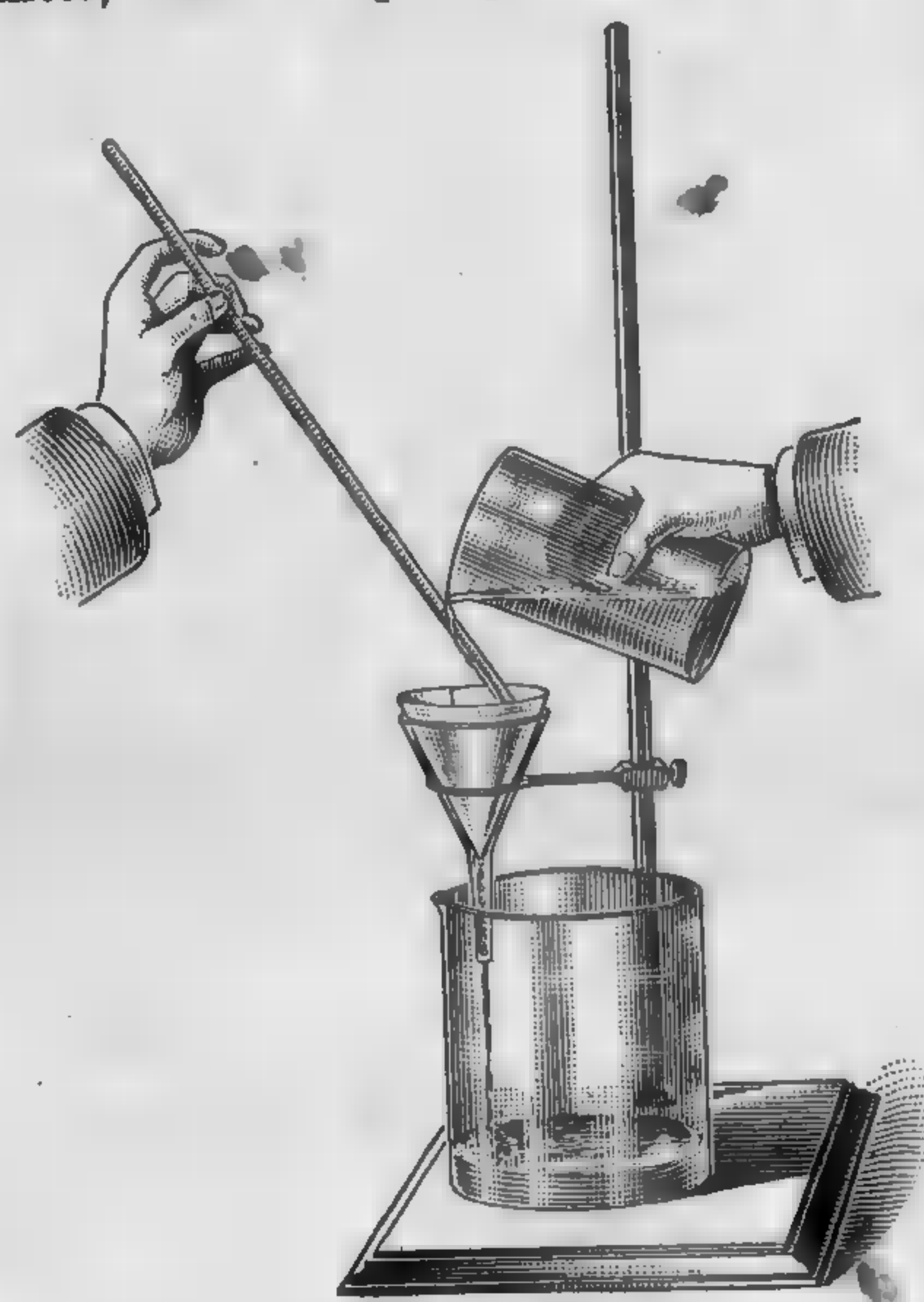


FIG. 8

When cold, filter these off, wash with cold water, and dry at a gentle heat.

Separation by crystallization is a process largely used for manufacturing purposes and is frequently met in practical work.

44. Distillation.—In the experiment made by evaporation, only solids that remain behind were dealt with, but in many cases it is the liquid that it is desired to obtain. In the laboratory, where pure water is an essential, it is obtained by the process of **distillation**, in which the steam is again condensed and collected.

43. Crystallization. Where two bodies are mixed together, both of which are soluble in water, but in different degrees, another plan may be adopted for their separation.

EXPERIMENT.—Take a mixture of about equal parts of potassium chlorate and potassium chloride. Place some in a test tube, and add sufficient water to dissolve the whole on boiling; now allow the solution to cool; tabular crystals consisting of the less soluble potassium chlorate will separate out.

EXPERIMENT.—Take either an ordinary flask fitted with stopper and delivery tube, or, preferably, a flask with side tube, as shown at *A B*, Fig. 9. Half fill it with brine to which a few drops of coloring matter (ink will do nicely) have been added; fix it in the retort stand and, as shown, connect the tube *B* by a piece of rubber tubing to a Liebig's condenser *C D*. The condenser consists of two glass tubes, one fitting inside the other; the steam passes through the inner one, and, as condensed, runs into the flask *G*, placed as a receiver. Through the outer tube a current of cold water is passed, which rapidly condenses the steam. The pipe *E*, conveying the water, is attached to the lower end of the condenser; by pipe *F* the overflow water is led to a drain or into a pan or pail placed

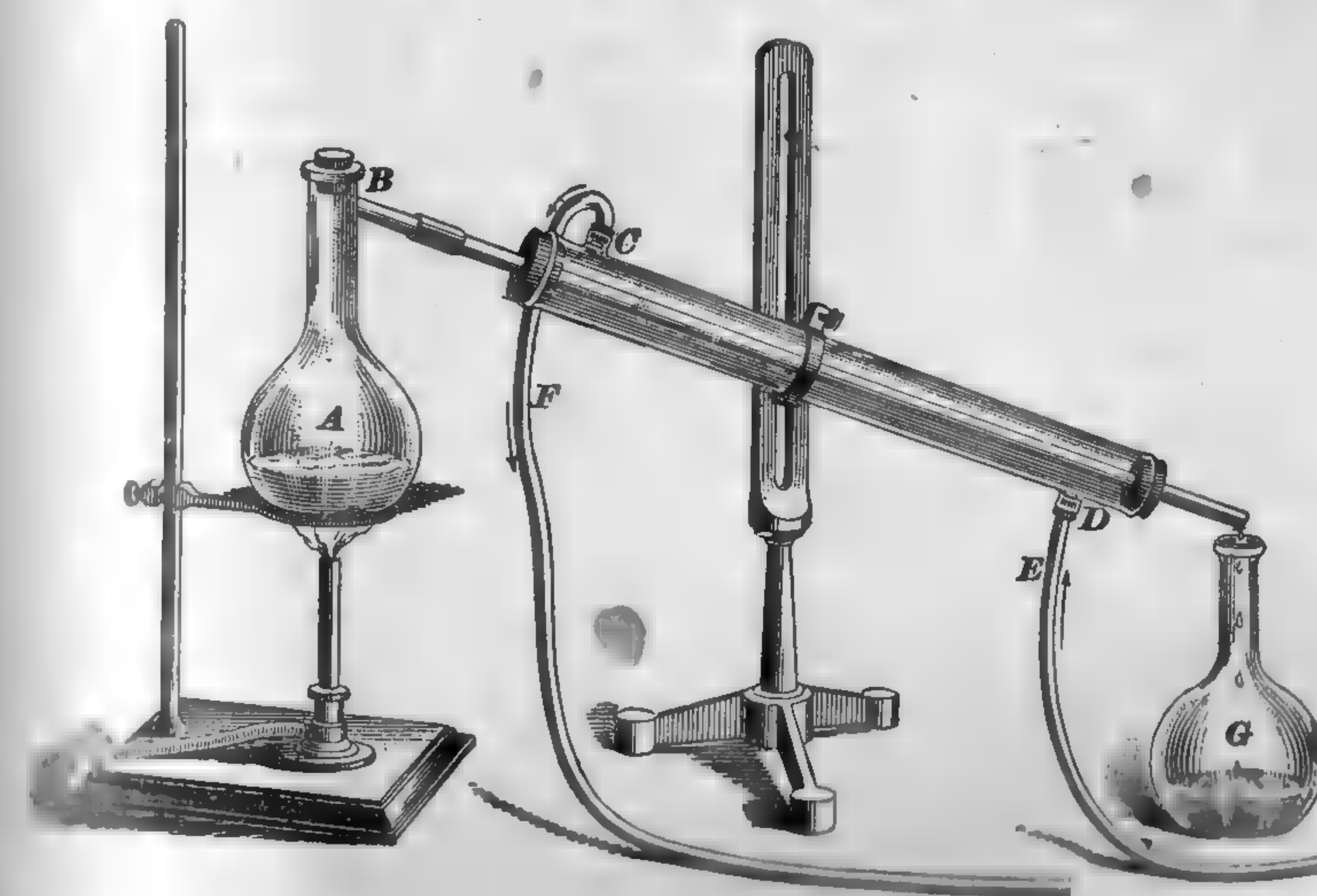


FIG. 9

conveniently. After some water has collected in the receiver, taste it, and observe that it is perfectly free from salt and coloring matter.

45. Sublimation.—Sublimation is a process somewhat analogous to distillation; it is, in fact, distillation of substances that condense into the solid instead of the liquid state.

EXPERIMENT.—Heat a small portion of a mixture of sand and ammonium chloride in a test tube; dense white fumes are evolved, which condense as a white crust in the upper part of the tube, the sand remaining behind.

Bodies that distil or sublime are called *volatile*; those that neither distil nor sublime are said to be *fixed*.

46. Ignition.—Occasionally the chemist makes use of the combustibility of bodies, and burns them off from others that are not combustible.

EXPERIMENT.—Mix some sand and lampblack, place some of it on a piece of platinum foil, and keep at bright red heat with the Bunsen burner; the lampblack will soon burn off, leaving the incombustible sand behind.

It may here be mentioned that when the directions are given to *ignite* a body it simply means that it is to be heated intensely, but it does not always follow that it will burn.

47. Catalysis.—The term **catalysis** is given to a form of action by which a substance appears to exert a chemical effect without itself changing. Thus, hydrogen peroxide may be decomposed into water and oxygen by means of gold or silver, neither of which are altered in the least in the process of decomposition, but each exerts a catalytic action.

48. Effervescence, Deliquescence, Efflorescence.
Effervescence is the escape of a gas from a liquid in which it is either generated or has been held by pressure, as carbonic acid from dissolving marble or from soda water. *Deliquescence* is the dissolving of a substance in water, which it absorbs from the air. Such substances are said to be *hygroscopic*, although all hygroscopic substances do not dissolve in the absorbed water. *Efflorescence* is the gradual crumbling of a crystal to powder on exposure to the air, due to the escape of the water necessary for the formation of the crystal.

49. Experiments.—Many of the experiments described in this and the following Sections are comparatively simple and may readily be performed. Some, on the other hand, are rather complicated and are usually confined to the lecture table. It is not necessary for the student to perform all the experiments described, but it is desirable that he should perform at least some of the simpler ones, for which he may have the apparatus and chemicals.

LABORATORY DIRECTIONS AND PRACTICAL HINTS

50. The room chosen for a laboratory should be of sufficient height, well lighted, and ventilated. It should contain a working bench or long table of hard and durable wood, some shelves for bottles and apparatus, gas for heating and lighting, and should, if possible, be close to a sink and water supply.

The student should, in the first place, make himself familiar with the names and uses of his apparatus. The bottles and jars containing chemicals, all properly labeled, should be so placed that they are easily accessible; they should not be allowed anywhere except in the place where they belong. The quantity that is required should be taken in a flask or test tube, and the bottle should be immediately restored to its proper place. A strict adherence to this rule will prevent the loss of time that otherwise would be spent in hunting all over the place for the desired substance, and will save confusion.

In getting the chemicals for an experiment, be sure that the right ones are taken; see that concentrated acids are not employed where dilute acids should be used, and never use C. P. (chemically pure) substances when the commercial ones will answer. Do not allow stoppers or corks to lie about or get mixed up. Take no more of the substance than you require, but if you happen to have an excess, do not return it to the bottle. It is better to throw it away, as the greatest confusion has been caused by chemicals being replaced in the wrong bottles.

When directions are given that substances should be mixed, solid bodies are first to be powdered in a mortar and then stirred together until the mixture is as uniform as possible.

Heat is applied by means of the Bunsen burner, and in heating test tubes the heat should be applied gently at first, with a constant rotary motion of the tube, or, if the tube is fixed, of the burner.

If heating a liquid, never let the flame play on the part of the tube above the surface of the liquid. When a solid is

heated, if any moisture happens to be present, it condenses in the upper and cooler parts of the tube; when there is the slightest sign of this, hold the tube almost horizontal, but with the hot part rather higher; this prevents the condensed water from running back on the hot glass.

A diary or notebook should be conscientiously kept, and every experiment, the changes noticed, and the results should be carefully entered. This applies with special force to weighing.

After you have finished your laboratory work, carefully wash all the apparatus used and wipe with a dry cloth any water from the retort stand or other apparatus that might rust.

Never use a piece of apparatus until you have carefully dusted it and have convinced yourself that it is perfectly clean.

INORGANIC CHEMISTRY

(PART 2)

HYDROGEN, AND OXYGEN, AND THEIR COMPOUNDS

HYDROGEN

Symbol H. Atomic weight 1.008. Density 1. Valence I. Specific gravity .0695. Molecular weight 2. One liter weighs .089873 gram.

1. History.—Hydrogen was discovered by Paracelsus in the 16th century. In the year 1766, Cavendish, an English chemist, investigated this gas more thoroughly, and gave it the name of *inflammable air*, and, by continued investigations, in 1781 proved its elementary character. Lavoisier, finally, gave it the name of *hydrogen*.

2. Occurrence.—To a certain extent, hydrogen occurs uncombined in nature. It is found in a number of volcanic gases. Bunsen, for instance, found that it formed nearly 45 per cent. of the gaseous exhalations of Nimarfjall in Iceland. Spectrum analysis further showed it to be a free constituent of the sun, as well as of certain fixed stars and nebulae. Graham obtained from the Lenarto meteorite—an exceptionally pure iron—3 times its own volume of hydrogen. The chief source of hydrogen is water, a compound which consists of 8 parts of oxygen combined with 1 part of hydrogen; it is also met with in *petroleum*, *bitumen*, and all animal and vegetable tissues.

3. Preparation.—The attraction of the metals sodium and potassium for oxygen is so great that they readily decompose water, thus liberating the hydrogen it contains, which, with sufficient care, may be easily collected.

EXPERIMENT 1.—Drop a very small piece of sodium, about half the size of a small pea, into a basin filled with water; notice that it melts, and, rushing around on the surface for some time, becomes smaller and smaller and finally disappears. Next, place a piece of either filter paper or blotting paper on the surface of the water, and drop a fragment of sodium on the paper. It soon melts, and then takes fire, burning with an intensely yellow flame.

Drop a piece of potassium, about the same size as the piece of sodium, in water; it at once takes fire and burns with a flame of a characteristic violet hue. (In this case the use of filter paper is unnecessary.)

The combination of sodium and potassium with oxygen, under these circumstances, is accompanied by considerable heat, which inflames the hydrogen gas liberated from the water by action of the metal. It is this gas that produces the flame; the characteristic tint in each case is due to the presence of the vapor of each metal.

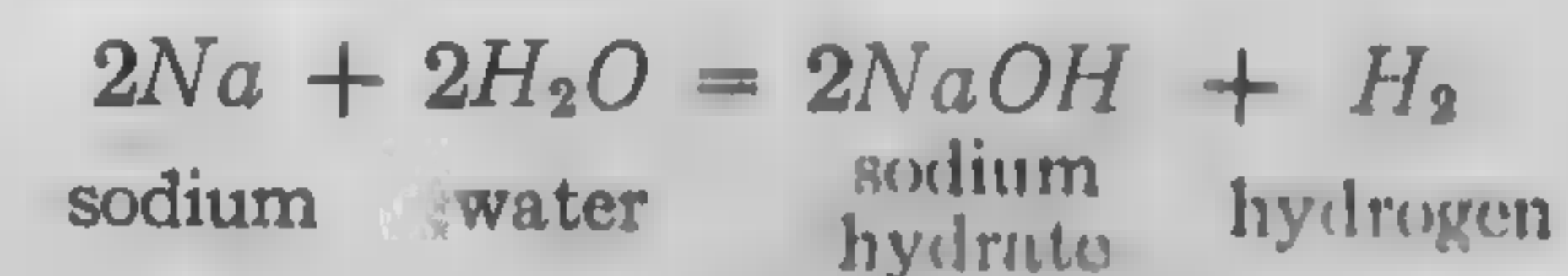
In any of these experiments with sodium or potassium and water, in which the escaping gas should take fire, stand some little distance off until it has burned out, and then wait until the molten metal, which first floats on the surface of the water, is dissolved; at this moment there is always a slight spit, so that, if you are standing immediately over it, there is danger that portions of the flying metal may get in your eyes and hurt them seriously.

It would be advisable for the student to omit these experiments for the present, and satisfy himself with carefully reading and studying them.

If the fragment of sodium or potassium, instead of being allowed to float on the water, is held under the surface of it by means of a pair of forceps, bubbles of gas are seen to rise; these consist of hydrogen, and may be collected in the following manner: First, fold a piece of wire gauze into a cone, in exactly the same way as previously directed to fold filter paper. Have a pair of tongs by which you can hold this cone point upwards under the water. Place in the water basin a glass jar, inverted and full of water, ready for collecting the gas; be quite sure that

not one bubble of air remains in the jar; that is, fill the jar with water until it overflows, close the mouth with a piece of plate glass, and quickly turn it upside down, immersing the mouth of the jar in the water of the basin; then remove, while thus submerged, the glass plate, and rest the jar's mouth on the bottom of the basin. Throw a piece of sodium, about the size of a pea, in the water of the basin, and at once depress it beneath the surface, with the gauze cone held in the tongs like a candle extinguisher; the point of the cone must be at least $\frac{1}{2}$ inch below the surface of the water. Wait until after the first bubbles of gas have risen; then hold the jar, without lifting it out of the water, over the point of the cone under which the sodium is decomposing the water, and collect the rising bubbles. Repeat this operation with a fresh piece of sodium, if necessary, until the jar is filled, that is, until all the water it contained has been driven out, or displaced, by the evolved hydrogen. Then lift the jar out of the basin, mouth downwards, and apply a lighted match to the gas in the jar; you will notice that it burns with a peculiar pale flame, tinged with yellow. This yellow hue is due to the sodium vapors that have been collected, incidentally, with the hydrogen.

The chemical reaction, representing the evolution of hydrogen, may be expressed thus:



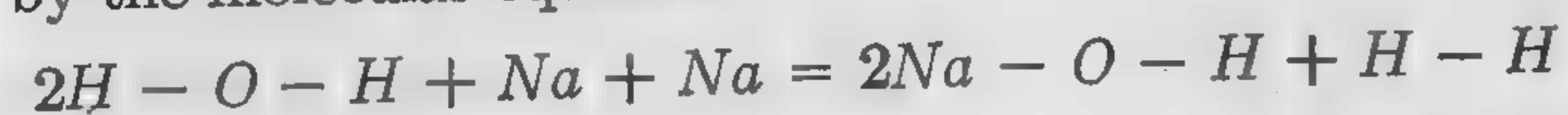
EXPERIMENT 2.—Take another small fragment of sodium, and dissolve it by throwing it into a small quantity of water in an evaporating dish; when the action is over, observe the soapy feeling that the water possesses and imparts to your fingers; this is characteristic of the class of bodies of which sodium hydrate, which has been formed according to the above equation, is a member. Evaporate the water by placing the dish on a tripod, protecting the dish from cracking by first placing a piece of wire gauze on the tripod, and applying heat; notice that, after the water has evaporated, a white, solid substance is left behind.

Sodium hydrate, popularly known as *caustic soda*, or *soda lye*, shows by its formula that it contains 1 atom of hydrogen; in fact, it may be regarded as water in which one of the atoms of hydrogen has been replaced by 1 atom of sodium. This

reaction, if the molecules are disregarded, may be represented by the equation



or by the molecular equation

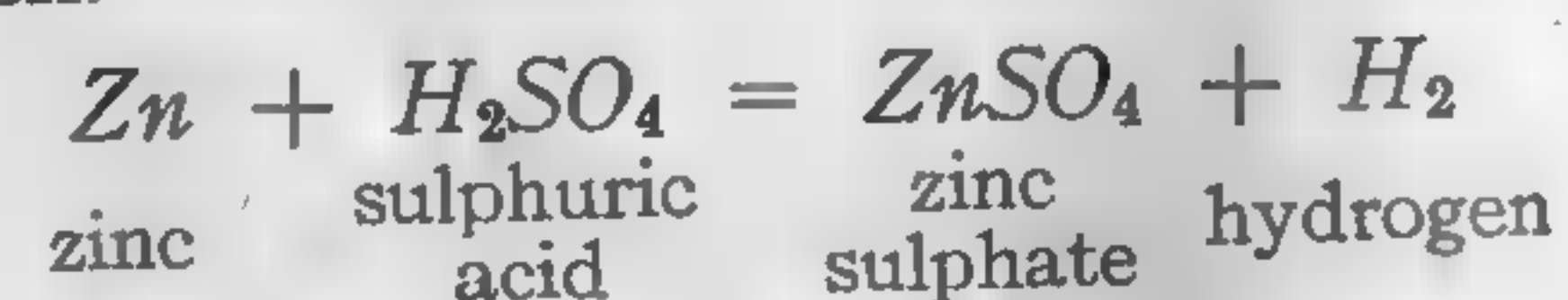


This reaction depends on the substitution of an atom of sodium for one of the atoms of hydrogen in water, and therefore is sometimes called *substitution*. The reaction is due to the different degrees of attraction that the different atoms have for one another. It thus appears that the relative attraction of the atoms for each other is an important matter. This is a very common kind of reaction, and is really a form of metathesis.

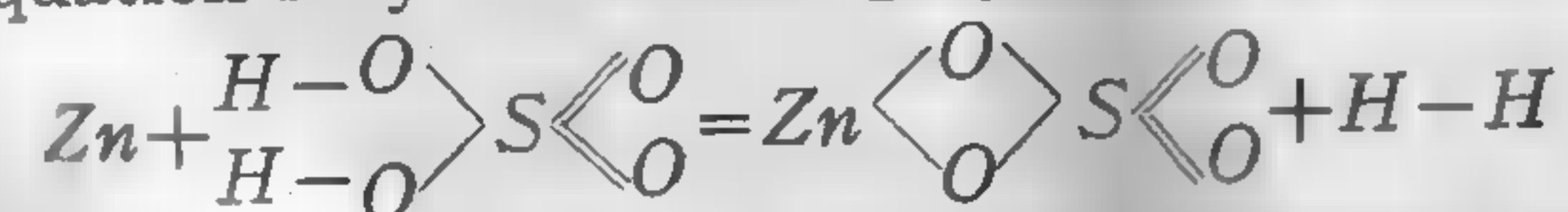
Hydrogen may also be prepared by the electrolysis of water as described in Art. 35, Experiment 2.

4. The most convenient method of preparing hydrogen consists of acting on either granulated zinc or iron with dilute sulphuric or hydrochloric acid; as a rule, zinc and sulphuric acid are employed. The gas comes off readily at the ordinary temperature if commercial zinc and acid are used; with chemically pure materials the reaction is slow in starting.

Chemically pure zinc is very slowly attacked by dilute acids. The addition of a few cubic centimeters of a dilute solution of copper sulphate or mercuric chloride aids the ready solution of the pure zinc in dilute acids with the rapid and uniform generation of hydrogen.



This equation may be written graphically as follows:



When the zinc first replaces the hydrogen atoms they are in the uncombined, or nascent, condition for an instant, during which time their activity is greatly increased; they immediately unite, however, and form a molecule of hydrogen.

The following experiment should be performed by the student:

EXPERIMENT.—Place $\frac{1}{2}$ ounce of granulated zinc in a wide-mouthed bottle (see Fig. 1) having two holes through the stopper that closes it. Through one of these openings a funnel tube passes to the bottom of the bottle, and through the other a delivery tube to the pneumatic trough, terminating, after passing through a beehive shelf beneath an inverted cylinder or jar filled with water, which rests on the beehive shelf. On

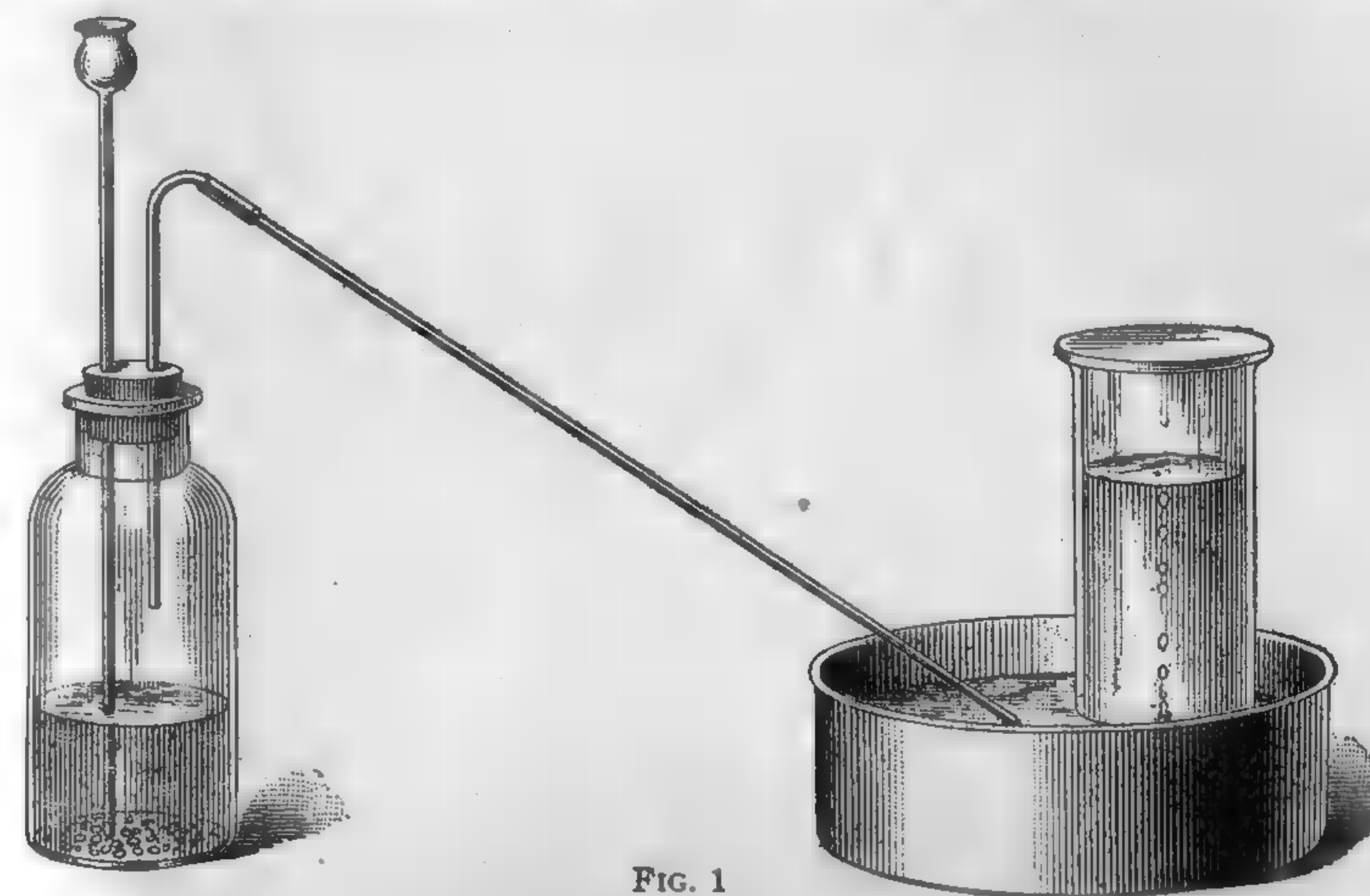


FIG. 1

pouring dilute sulphuric acid—1 part of the commercial acid and 6 parts of water, and cooled by placing the glass containing the acid solution in a basin filled with cold water—through the funnel tube upon the zinc, effervescence occurs, and bubbles escape from the delivery tube. Do not, however, add much acid at a time or the action will become too violent, the mixture will become too hot, and will froth through the funnel tube; should there be any indication of this, pour a little water into and also on the outside of the flask, in order to cool it.

Care should be taken that all the air is expelled from the flask and glass tubing before the hydrogen is collected. It is therefore recommended not to place the collection jar in its place until all the air is driven out by the evolved hydrogen. This is easily ascertained by filling a small test tube with the gas, and by trying whether it burns quietly when a light is brought close to the mouth of it. (The tube must, owing to the lightness of hydrogen, be held with the mouth downwards.) If all the air has been expelled from the apparatus, the gas will burn quietly; if not, it will ignite with a detonation.

If the direction is given to collect a gas over the pneumatic trough, it is meant that the gas must be collected under water.

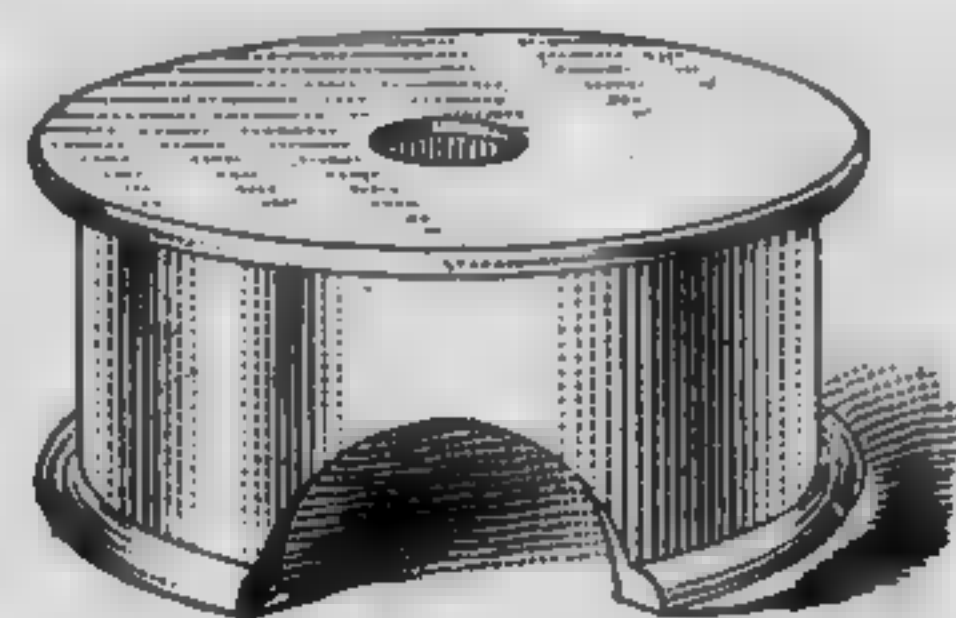


FIG. 2

For this purpose a large basin, or pan, is half filled with water, the beehive shelf, Fig. 2, is placed in the pan, and the delivery tube led into the side opening of the shelf; the jar in which the gas is to be collected is filled with water, inverted, and placed over the top opening of the beehive shelf, Fig. 3.

5. Properties.—Hydrogen is a colorless, odorless, and tasteless gas, and is the lightest substance known. It is 14.43 times lighter than air, 11,000 times lighter than water, and 240,000 times lighter than platinum. It is very slightly soluble in water, 100 volumes dissolving only 2.15 volumes at 0° of the gas, and is used as the standard of density, molecular weight, and volume of gases and vapor. It passes with great ease through animal and vegetable membranes, as well as through porous substances that are impervious to water.

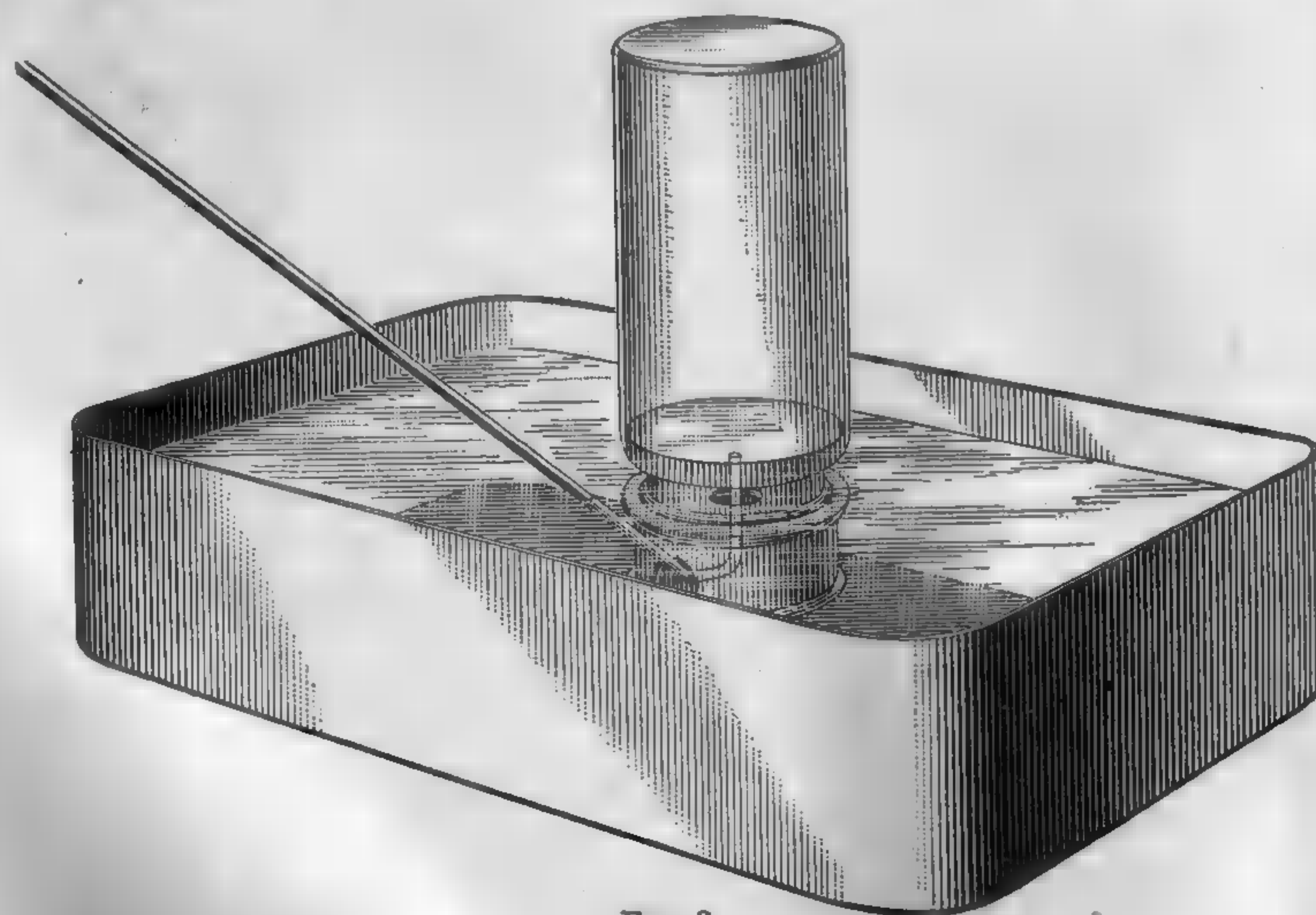


FIG. 3

It cannot be preserved in any vessel having the slightest crack or flaw, or it will pass through it with a much greater readiness

than air. This property is expressed by saying that hydrogen is very *diffusible*.

Hydrogen in many ways behaves as a metal; it is, for instance, the only gas that shows a noticeable property of conductivity of heat, and it has, consequently, been repeatedly proposed to class it among the metals.

In order to liquefy a gas, it becomes necessary that its molecules shall manifest a certain degree of cohesion, or, in other words, that the amplitude of molecular movement shall be arrested as far as possible. As this amplitude of molecular movement depends, more or less, on the temperature to which the gas is subjected, it follows that for every known gas there is a certain temperature above which liquefaction cannot take place, regardless of the pressure applied to the gas; this temperature is known as the *critical temperature*.

The critical temperature of hydrogen (which is $-238^{\circ}\text{C}.$) lies 35° above the absolute zero ($-273^{\circ}\text{C}.$), which means that at or below this temperature it may be obtained in the liquid state by subjecting it to sufficient pressure, while at a higher temperature no pressure will liquefy it. About 15 atmospheres pressure would probably be required at the critical temperature, but if the temperature is still further depressed, less pressure will be required. By subjecting hydrogen to pressure at very low temperatures, it may even be solidified.

In 1898, Dewar succeeded in liquefying hydrogen in sufficient quantities to learn the properties of the liquid. It is colorless and boils at $-252.8^{\circ}\text{C}.$ Its specific gravity as compared with water is .07, this, being much less than any other liquid.

By its own rapid evaporation liquid hydrogen is frozen to a white solid mass, melting at $-257^{\circ}\text{C}.$ By the rapid evaporation of this solid the lowest temperature reached $-260^{\circ}\text{C}.$, has been obtained. Without exception, all the known gases have been liquefied by means of liquid hydrogen.

Among other physical properties that hydrogen possesses must be mentioned its remarkable faculty of passing through plates of iron and platinum at elevated temperatures. According to Graham, who thoroughly investigated this phenomenon, and named it *diffusion*, this faculty is closely related to the

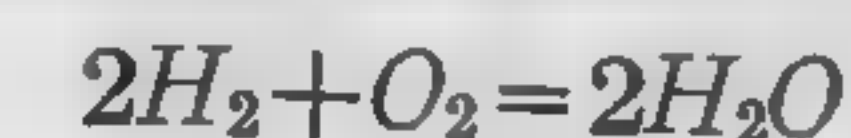
property possessed by a number of solid bodies, and particularly metals, such as platinum, iron, and palladium, of absorbing hydrogen. Palladium, especially, is distinguished by its energy to absorb, or *occlude*, hydrogen. Graham has shown that there is no necessity of assuming porosity in the structure of the metals to account for this phenomenon, but that it is due to the fact that such metals absorb the hydrogen and yield substances that still retain characteristic metallic properties, but readily evolve part of the absorbed gas when heated. The last traces, however, can be driven off only at a red heat in vacuo. After the absorption of hydrogen the metal presents the same appearance as before, but some of its physical properties are slightly changed. Thus, in the case of palladium, the metal becomes more magnetic and its electric conductivity is reduced. As our present knowledge proves the absence of any metallic character in either liquid or solid hydrogen, this is not an alloy. At a red heat palladium will absorb or *occlude*, 900 times its own volume of hydrogen, with an increase of 1.6 per cent. in the volume of this metal. To this absorbed form of hydrogen Graham gave the name *hydrogenium*, concluding that although the hydrogen did not combine chemically with the metal, it did assume the solid form, acting as a semimetal giving rise to an alloy such as is obtained when sodium and mercury are brought together.

At one time it was supposed that the hydrogen united with the palladium in a definite ratio and formed a compound having the formula Pd_2H , or even Pd_3H_2 . Later investigations have shown, however, that these substances are simply a mixture of two non-miscible solids, the miscibility of which increases with the temperature.

6. Hydrogen is a combustible gas which, when heated to $500^\circ C.$, becomes capable of uniting with the oxygen of the air, with the evolution of light and heat. It burns with a non-luminous and almost colorless flame at ordinary pressure, but its luminant power is increased as the atmospheric pressure is increased. Though non-luminous at ordinary temperatures, its flame evolves a great amount of heat. It

is combustible, but not a supporter of combustion; a lighted candle plunged into a jar filled with hydrogen is at once extinguished. It does not support respiration—animals lose life when confined in it; it should, however, not be assumed from this fact that the gas is poisonous, for the cause of death is simply a deprivation of the oxygen necessary to animal life.

Water is the sole product of the combustion of hydrogen in atmospheric air or oxygen, hence its name hydrogen, which is derived from the Greek words meaning *water producer*.



As all gases obtained from mixtures in which water is present contain a certain quantity of aqueous vapors, it is necessary to dry the hydrogen before attempting to prove the presence of water as a result of its combustion. This is accomplished by passing the gas that is to be dried over some substance that possesses a strong affinity for water. The most important *desiccating* or *drying agents* used in the laboratory for drying gases, liquids, and solids are *granulated calcium chloride* and *strong sulphuric acid*. Which of these is the

more suitable depends, of course, on the nature and properties of the gas to be dried; hydrogen, for instance, may be dried by being passed through either calcium chloride or sulphuric acid.

(If the student should attempt to perform the following experiment, great care should be taken to avoid an explosion, and he should take great pains to follow all the directions minutely.)

EXPERIMENT 1.—Choose a piece of glass tubing of about $\frac{1}{2}$ -inch bore and about 10 inches long, and fit a stopper to each end. To one stopper fit a tube bent at right angles, with the end drawn out to a fine point, so as to form a jet; through the other pass a piece of tubing bent to the shape shown in Fig. 4. Fill the large tube with small pieces of calcium chlo-

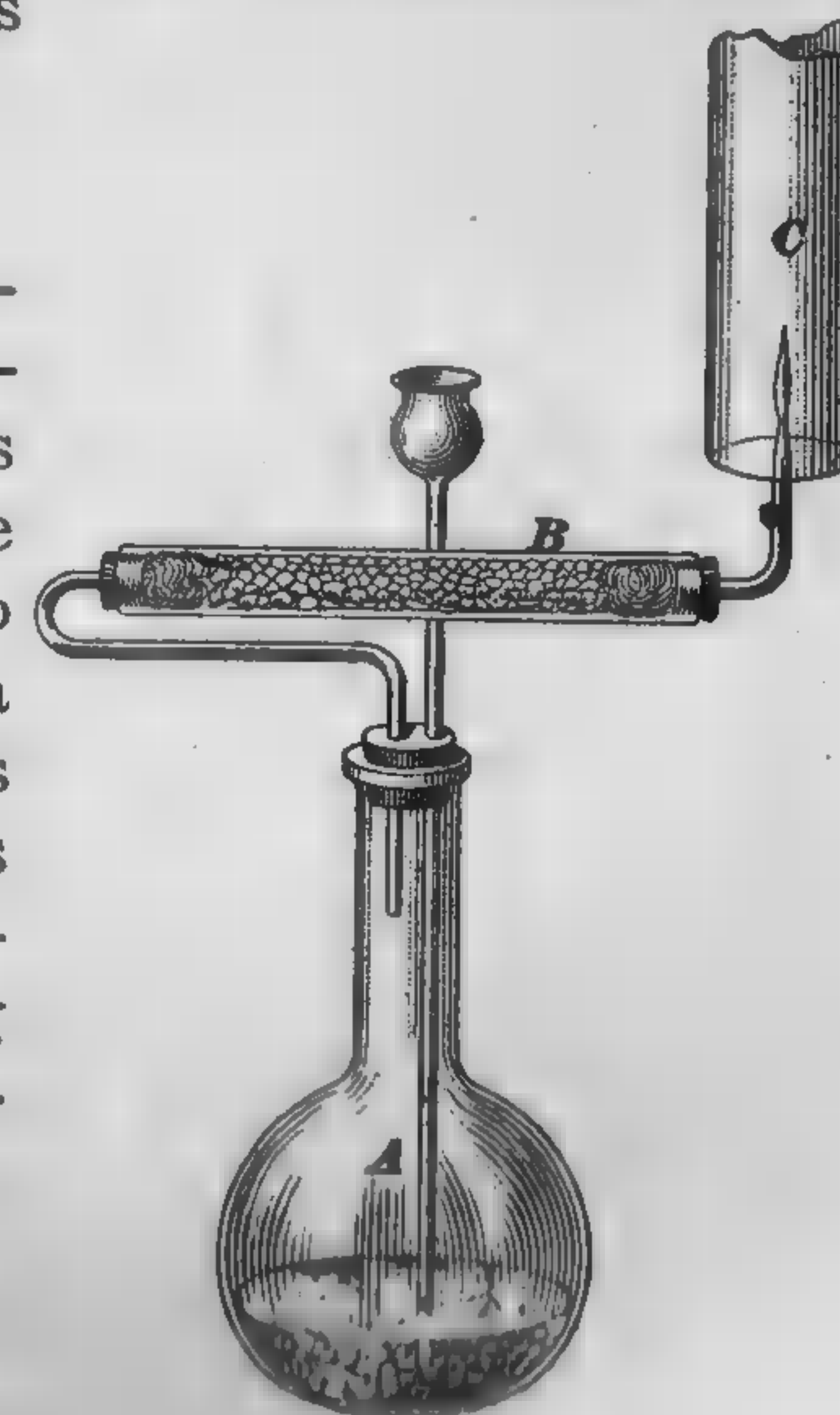


FIG. 4

ride, and place at each end, between the chloride and the stopper, a plug of cotton. A slow current of gas passed through this apparatus will emerge in the dry state. If necessary, place some more zinc and sulphuric acid in the generating flask *A*; let the gas escape until a test tube collected burns quietly without explosion; then attach the drying tube *B*, and after a few seconds light the gas as it issues from the jet *C*.

Take a glass tube *C*, about 15 to 18 inches long and about $\frac{1}{2}$ inch in diameter; dry the inside by pushing through it a plug of cotton; hold it over the burning jet; the watery vapor produced by the ignition of hydrogen in air condenses in the cooler parts of the tube.

Too much stress cannot be laid on the injunction to **first see, before** lighting the jet, that a collected test tube of the gas burns quietly. The neglect of this fact will lead to an **explosion**.

This experiment is often accompanied by a peculiar musical note, produced by a rapid series of small explosions within the long tube. The moisture that condenses on a kettle, or other vessel filled with cold water and heated over a gas flame, is the product of combustion of the hydrogen of the coal gas.

Owing to its lightness, hydrogen is used for the purpose of filling balloons. The amount that a balloon will carry, that is, its ascensional power, is the difference between the weight of the balloon itself with its contained hydrogen, and the weight of an equal volume of air. One liter of hydrogen possesses an ascensional force of 1.2 grams; the following experiment is illustrative of this property:

EXPERIMENT 2.—Take a jar of hydrogen, and, setting it down mouth upwards, take off the glass cover; after the expiration of about $\frac{1}{2}$ minute, apply a match; the gas will be found to have entirely escaped. Take a second jar, and, holding it mouth downwards, remove the closing glass cover; let it also remain about $\frac{1}{2}$ minute and apply a light; the gas will burn as usual, but little of it having escaped.

7. Summary.—Hydrogen is principally found in water. It may be prepared by the action of certain metals on that liquid, as sodium or potassium; also, by the action of zinc or iron upon acids. It is a colorless, tasteless, and odorless gas, inflammable, and a non-supporter of respiration or combustion. It is the lightest body known.

8. Laboratory Directions.—It must not be forgotten, in dealing with sodium or potassium, that the fingers and forceps must be *perfectly dry*.

Great care should be taken in diluting sulphuric acid; **on no account add water to sulphuric acid**. In diluting sulphuric acid, add the acid to the water in very small proportions very slowly (drop by drop).

Never omit the precautionary measures previously given before lighting a jet of hydrogen.

In handling chloride of calcium, place it in the drying tube as quickly as possible; do not expose it unnecessarily to the air, and replace the stopper in the bottle containing it immediately; otherwise, it will absorb moisture.

Experiments 1 and 2 of Art. 3 and Experiment 1 of Art. 6 are usually confined to the lecture table; study the apparatus, general arrangements, and results carefully.

OXYGEN

Symbol O. Atomic weight 16.00. Density 15.88. Valence II. Specific gravity 1.1056. Molecular weight 32. One liter weighs 1.429 grams.

9. History.—Doctor Priestley, of Birmingham, England, discovered, in 1774, that by heating mercury in contact with air in a closed vessel the amount of air present was lessened, and that red scales were formed on the surface of the mercury; he found that the red scales thus produced consisted of mercury and a gas which he named *dephlogisticated air*. The following year, 1775, Scheele, a Swedish chemist, discovered, independently, the same gas, which he named *empyrean air*. Condorcet called it *vital air*, and, in 1781, Lavoisier named it *oxygen*, from the Greek words for *acid former*. Up to Lavoisier's time, the phlogiston theory, proposed by Stahl, was generally accepted. According to this theory, every combustible substance contained something called phlogiston, which in escaping caused the phenomenon known as combustion, or burning. It was from this theory that Priestley derived his

name for oxygen, and though he proved its elementary character, the name indicates that he did not well understand its real nature. Lavoisier disproved the phlogiston theory and showed that combustion is a union with oxygen.

10. Occurrence.—Oxygen is the most abundantly occurring element in nature; it exists free in the air, of which it forms about one-fifth. Combined with other elements, it constitutes two-thirds of the entire globe. Water alone consists of eight-



FIG. 5

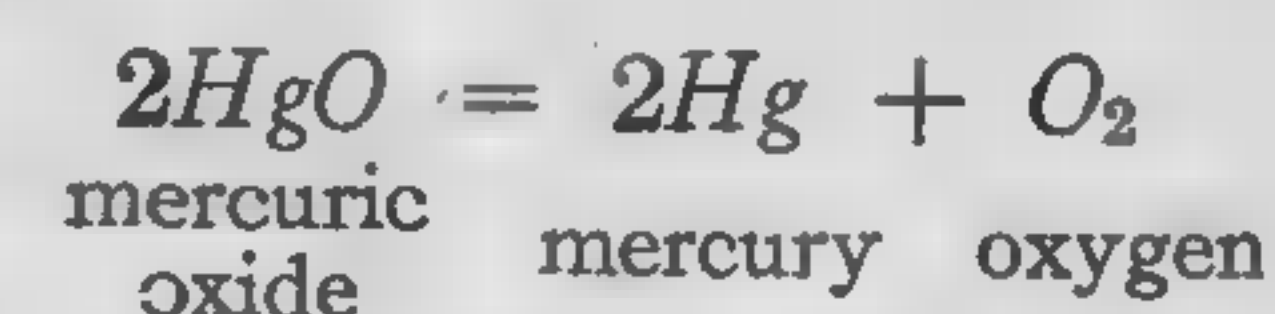
ninths of oxygen; and fully one-half of the weight of all minerals, three-quarters of the weight of all living beings, and nearly four-fifths, by weight, of all plants is oxygen.

11. Preparation.—Many methods have been suggested for the preparation of oxygen. In this Section will be given only a few of the most important.

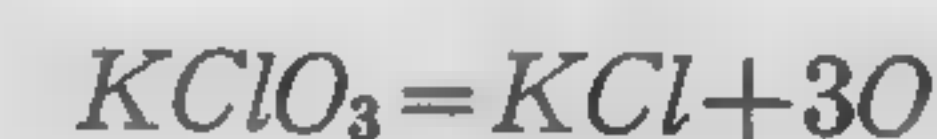
EXPERIMENT 1.—A small quantity of mercuric oxide is heated in a test tube A, Fig. 5, which, presently, becomes lined with a mirror of metallic mercury, which after a little while separates into little drops; if a match

or wax taper, previously lighted and extinguished, but still bearing a spark at the end, is thrust into the mouth of the tube, it instantly bursts into flame and burns with great brilliancy.

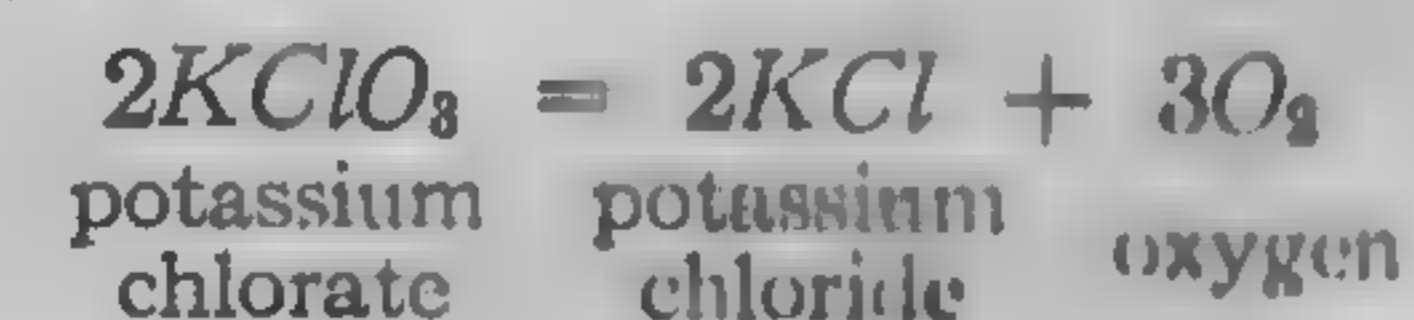
This effect is due to a gas that is being disengaged and, to use Lavoisier's own expression, it is "eminently fitted to support combustion." In other words, it is oxygen, which is produced by a very simple reaction; that is, the mercuric oxide has been decomposed by heat into mercury and oxygen, according to the equation



Most of the methods employed for the preparation of oxygen are instances of direct decomposition. The substance most frequently used is potassium chlorate, which is a compound of potassium, chlorine, and oxygen. At a comparatively low temperature the oxygen is driven off from this body, a compound of potassium and chlorine remaining behind.



This equation represents only the manner of the reaction and the accompanying relative quantities by weight. Remembering that free atoms do not exist, but are always combined in molecules and that oxygen is diatomic, the equation written molecularly would be



This equation written graphically would probably be



From this it would appear that chlorine, which, when combined with hydrogen, or, as in the present case, when united with potassium alone, is monovalent, when united with oxygen appears to be pentavalent in this case, thus furnishing a good illustration of variable valence.

EXPERIMENT 2.—Use the same apparatus as that employed in the last experiment, Fig. 5, place in the test tube about enough potassium

chlorate to fill the bottom of the tube $\frac{1}{2}$ inch, and apply heat gently to it. At first the salt crackles; this is owing to the crystals being split up by the heat, and is known as *decrepitation*. The chlorate soon melts, and then appears to boil; the salt is really decomposed owing to the disengagement of oxygen, as is easily proved by applying the spark test.

If, instead of using potassium chlorate alone, a mixture of that salt with about one-quarter of its weight of manganese dioxide (black oxide of manganese) is employed, the gas is evolved much more rapidly, more uniformly, and at a much lower temperature. The mode in which this oxide acts is at present obscure; it is, however, probable that it is converted

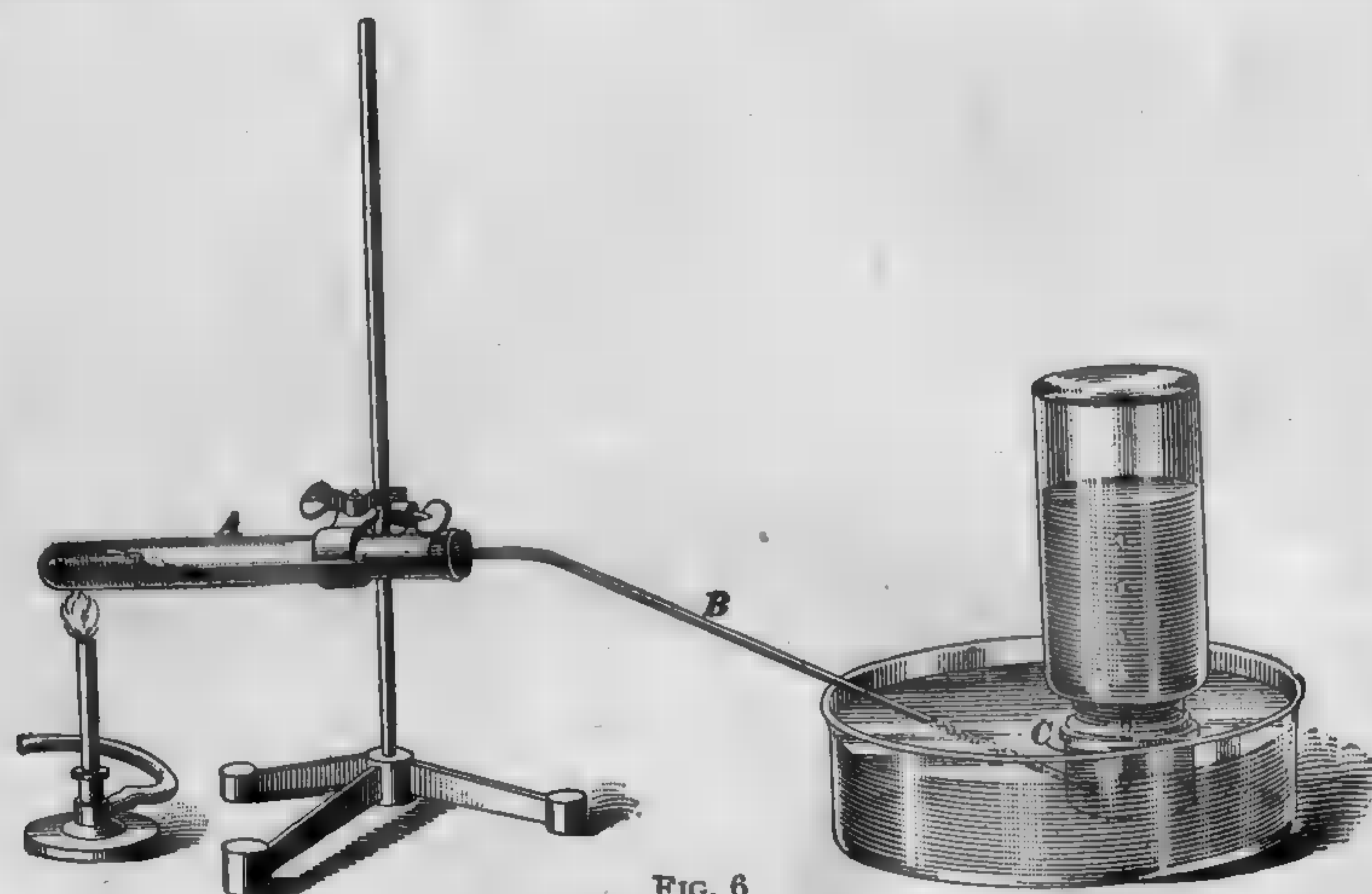


FIG. 6

into an unstable, higher oxide, which is continually formed and decomposed during the reaction. At the end of the experiments the manganese dioxide is always found unaltered. This method of preparing oxygen is the one usually employed in laboratories, except when the oxygen is required in a state of absolute purity.

The student will require seven jars of oxygen to perform the following experiments. It will be found that the most convenient way is to prepare two jars of the gas at a time.

EXPERIMENT 3.—Fill a 6-inch test tube about one-third with the mixture of potassium chlorate and manganese dioxide in the proportion men-

tioned before; this amount is sufficient to evolve the quantity of oxygen required. Push a wire down to the bottom of the tube, so as to make a free passage for the gas. Connect the test tube *A*, Fig. 6, to a delivery tube by means of an air-tight fitting stopper, and run this delivery tube *B* into the pneumatic trough to the side opening of the beehive shelf *C*; have in readiness three collecting jars filled to the brim with water. Holding the Bunsen burner in the hand, commence warming up the mixture gently at the top, that is, the end nearest the stopper, and slowly bring the flame nearer the bottom as the gas is evolved. The reason for this is that the mixture cakes on being heated; if heated first at the bottom, the upward current of gas would carry the loose dust of the mixture on with it, and probably choke the delivery tube. Withdraw the Bunsen burner when the third jar is about half full; then remove the end of the delivery tube from the trough; otherwise, as the hot gas within cools, the contraction will draw up the water and crack the test tube.

EXPERIMENT 4.—To one jar filled with oxygen add some water in which you have previously dissolved some lime (one-half of a test tube full of water is quite sufficient); see that the solution of lime is clear; shake the lime water and the oxygen up well, and observe that the lime water remains as clear as it was originally. Apply the spark test to the same jar after shaking up.

EXPERIMENT 5.—To the second jar filled with oxygen add a solution of litmus and shake up; notice that the blue color of the litmus solution remains unchanged.

EXPERIMENT 6.—In the third jar burn a piece of charcoal. Take a deflagrating spoon, fit over it a piece of cardboard or tin (the latter preferable), so that the spoon will reach to about one-third of the height of the jar from the bottom. Put the charcoal on the spoon and ignite it with the Bunsen burner; when glowing, plunge the spoon into the jar of oxygen until the cardboard covers the mouth of the jar; it burns brightly. When the combustion is over, remove the deflagrating spoon, pour in some lime water and shake up; notice that the lime water becomes milky.

If you shake a jar of oxygen with any kind of liquid, always cover the jar with a piece of plate glass; also, when you lift the jar from the pneumatic trough.

12. For the remaining experiments two more jars may be filled in the ordinary way over the pneumatic trough; another jar must be wiped perfectly dry and filled by *downward displacement*, that is, do not use the pneumatic trough, but place the jar in which you intend to collect the oxygen mouth upwards; lead the delivery tube to the bottom of the

jar and evolve the oxygen as has been already described. Oxygen, being somewhat heavier than air, will settle to the bottom of the jar and slowly drive the air out of it. If a glowing match or taper is applied to the mouth of the jar it will be at once relighted when the vessel is full of oxygen.

For the next experiment use a deflagrating jar; that is, a jar open at the top and bottom, in fact, simply a strong glass cylinder. Close the upper opening and fill the cylinder over the pneumatic trough with oxygen; allow it to stand in the pneumatic trough after it is filled until you use it.

EXPERIMENT 1.—Take a piece of watch spring; make it into a spiral and weigh it carefully. Next fasten it to a piece of cardboard, and attach

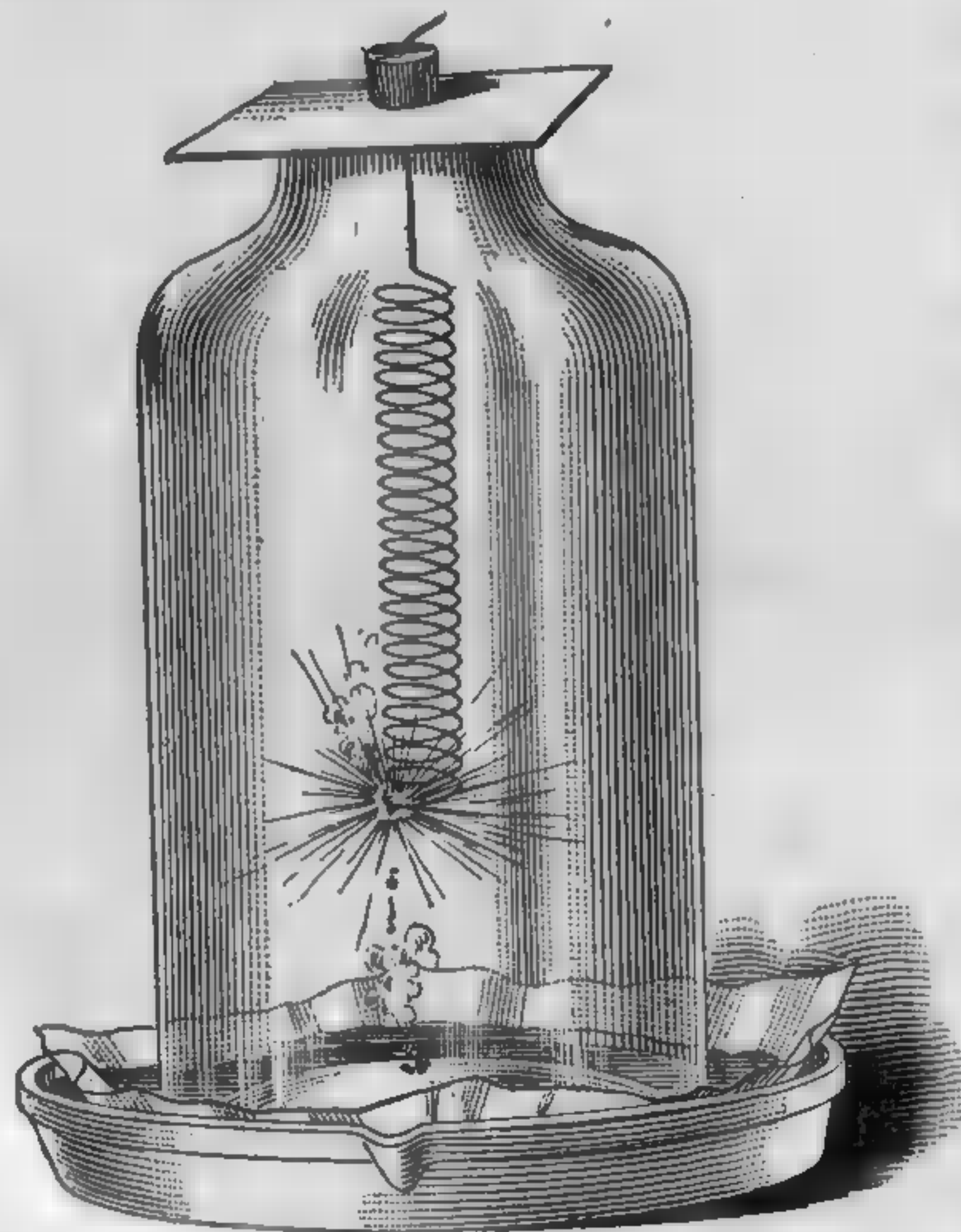


FIG. 7

to the other end of the spring a small piece of wood (a short piece of a match serves well). The watch spring is now ready for burning. The deflagrating jar, mentioned before, is then removed from the pneumatic trough into a flat porcelain dish, in the bottom of which a piece of writing paper has been placed and allowed to become saturated with the water in the dish. There will thus be about $\frac{1}{2}$ inch of water at the bottom, then the paper, and underneath that another thin layer of water. Loosen the stopper at the top, light the piece of wood attached to the spring, and drop the spring as quickly as possible into the jar, closing it with the piece of cardboard fixed to the end of the spring (see Fig. 7). You will notice that it burns brilliantly, throwing out a number of sparks, while from time to time drops of molten oxide fall to the bottom; these are so hot that if allowed to come in contact with the porcelain dish they would fuse into the glaze even after falling through an inch or so of cold water. The stiff writing paper momentarily arrests their fall and thus gives them time to cool. When the burning is over, remove the unburnt end of the spring; collect very carefully the whole of the globules of oxide of iron, place them in a crucible, and thoroughly dry them with a gentle heat. Weigh the oxide and the remainder of the iron; notice that there will be a sensible increase of weight over that of the

the other end of the spring a small piece of wood (a short piece of a match serves well). The watch spring is now ready for burning. The deflagrating jar, mentioned before, is then removed from the pneumatic trough into a flat porcelain dish, in the bottom of which a piece of writing paper has been placed and allowed to become saturated with the water in the dish. There will thus be about $\frac{1}{2}$ inch of water at the bottom, then the paper, and underneath that another thin layer of water. Loosen the stopper at the top, light the piece of wood attached to the spring, and drop the spring as quickly as possible into the jar, closing it with the piece of cardboard fixed to the end of the spring (see Fig. 7). You will notice that it burns brilliantly, throwing out a number of sparks, while from time to time drops of molten oxide fall to the bottom; these are so hot that if allowed to come in contact with the porcelain dish they would fuse into the glaze even after falling through an inch or so of cold water. The stiff writing paper momentarily arrests their fall and thus gives them time to cool. When the burning is over, remove the unburnt end of the spring; collect very carefully the whole of the globules of oxide of iron, place them in a crucible, and thoroughly dry them with a gentle heat. Weigh the oxide and the remainder of the iron; notice that there will be a sensible increase of weight over that of the

iron alone previous to the burning. The increase is due to the oxygen that is present in the iron oxide.

EXPERIMENT 2.—In another jar of oxygen, collected over the pneumatic trough, immerse, with help of the deflagrating spoon, a piece of sulphur, previously lighted over the Bunsen burner; notice the brilliant light with which the sulphur burns in the oxygen. Add to the jar, after the burning, some litmus solution; notice that this originally blue liquid is turned red.

EXPERIMENT 3.—In the other jar filled with oxygen burn a piece of phosphorus about the size of a small pea. It is one of the most brilliant experiments with oxygen. A very neat apparatus for this purpose is shown in Fig. 8. A light wire tripod has a ring at its upper part for supporting a globe that contains the gas, and just below it a shallow cup containing water, into which the neck of the globe enters. From the center of this cup rises a piece of wire, crowned with a small cup to serve as a receptacle for the phosphorus. The globe is filled about four-fifths with oxygen and then inverted on the stand. When all is ready, a piece of phosphorus is very thoroughly dried between two pieces of blotting or filter paper. The globe being raised, the piece of phosphorus is dropped into the receptacle, inflamed by touching it with a hot wire, and the globe replaced. The combustion is at once exceedingly vivid, but after a few seconds the phosphorus becomes volatilized by the heat, and burns throughout the entire volume of oxygen with a brilliancy almost inconceivable.

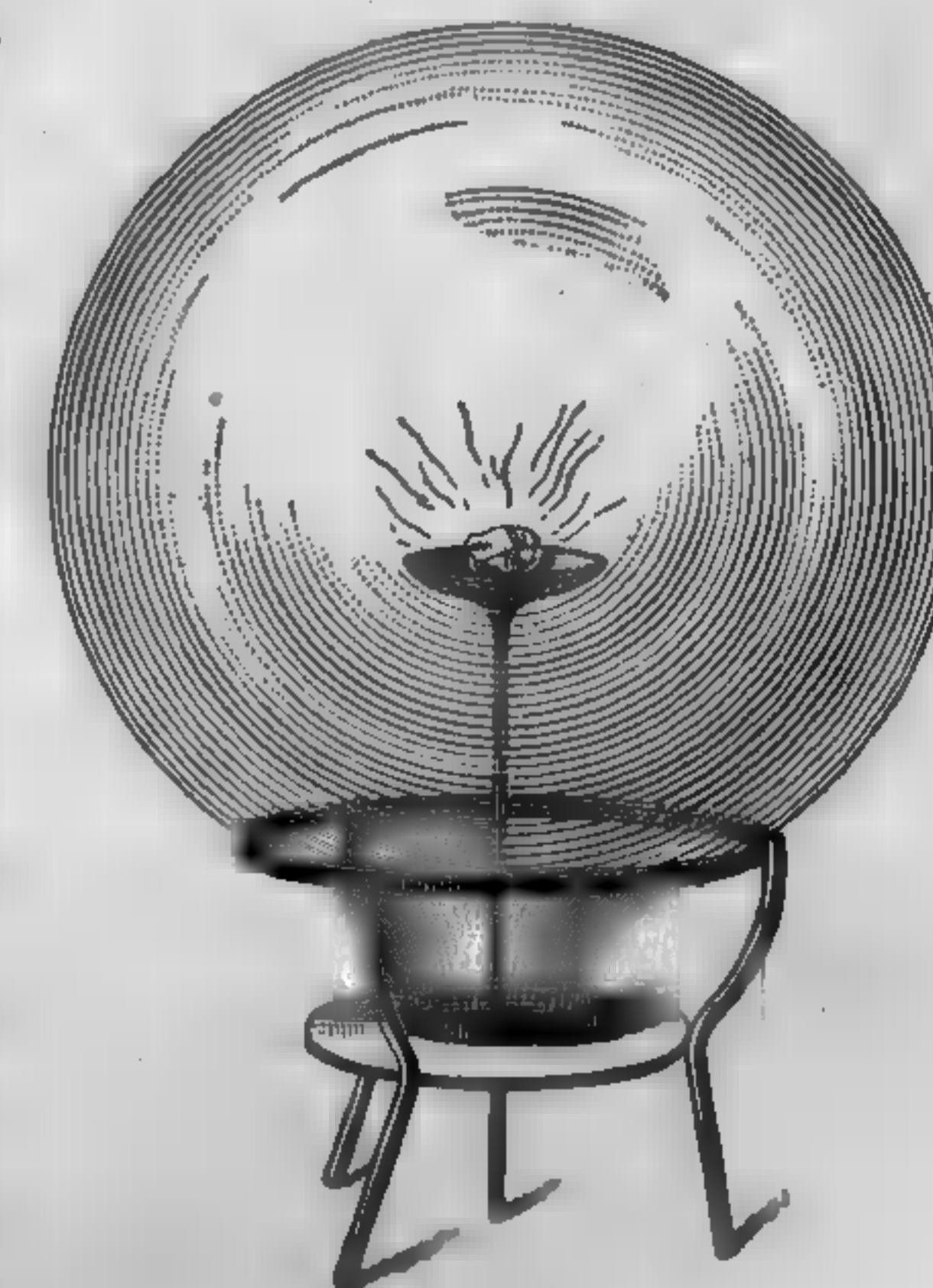


FIG. 8

EXPERIMENT 4.—In the jar of oxygen that has been obtained by downward displacement, a piece of metallic sodium is to be burned. Sodium possesses such an affinity for oxygen that it must be kept in some liquid that does not contain that element; naphtha is usually employed for this purpose. Cut off a little piece about the size of a small pea, being very careful that the knife and everything that touches the metal is perfectly dry. Place in a clean and dry deflagrating spoon, heat over the Bunsen burner until it just glows, then put it in the jar of gas; it burns brightly; the products of combustion, which are solid, remain in the spoon. Allow it to get quite cool, then place the spoon in a little water in a beaker and dissolve off the oxide of sodium. To some litmus solution in a test tube add just a drop of dilute sulphuric acid. Pour the red solution thus obtained into the beaker containing the oxide of sodium; the blue color of the litmus will be immediately restored.

13. On a large scale, oxygen is manufactured by a process devised by Brin. Air is forced into specially prepared porous barium oxide, BaO , at a temperature below redness, and barium dioxide, BaO_2 , is formed. The stream of air is cut off and the barium dioxide is heated to redness, the pressure in the apparatus being lowered by air pumps at the same time.

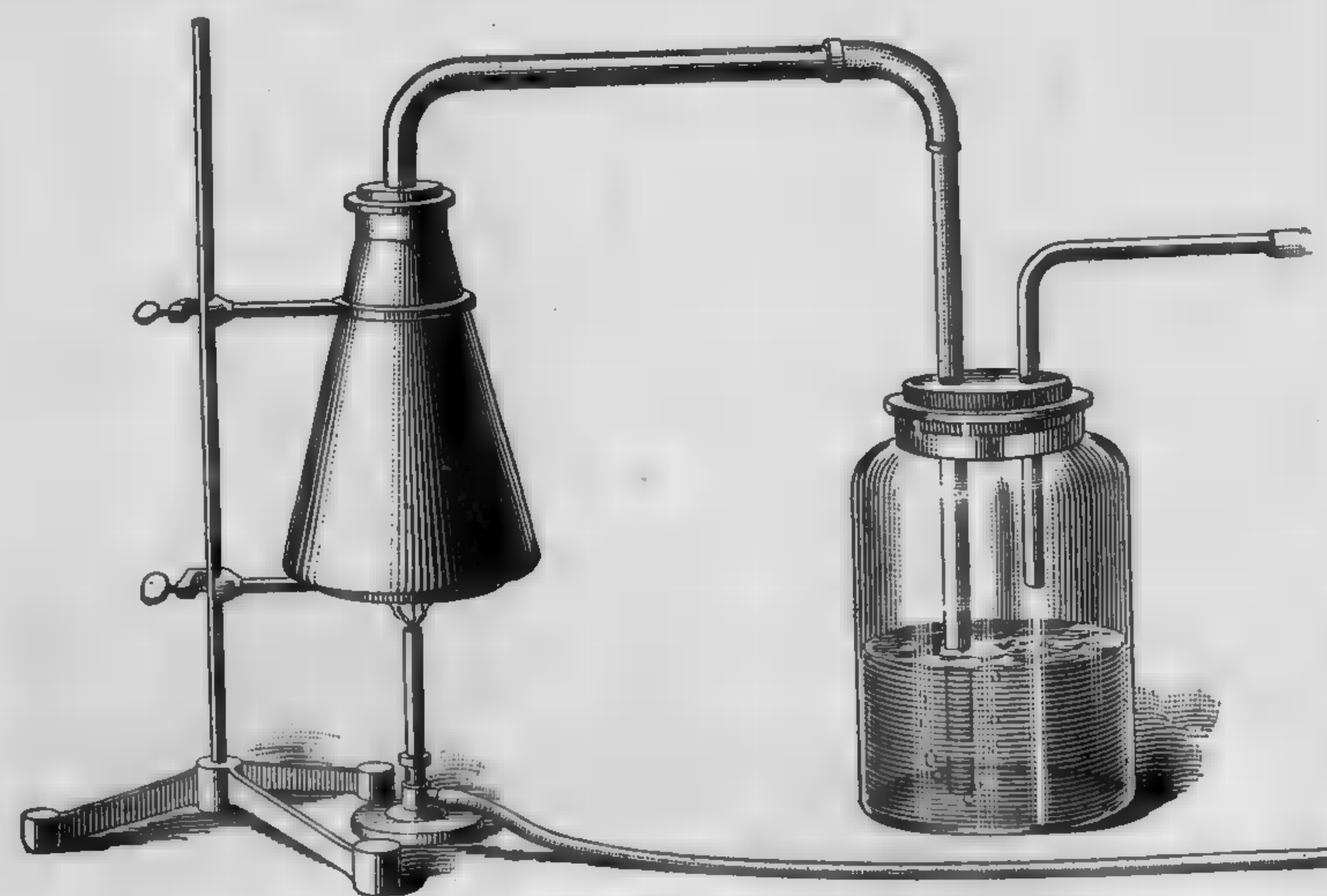
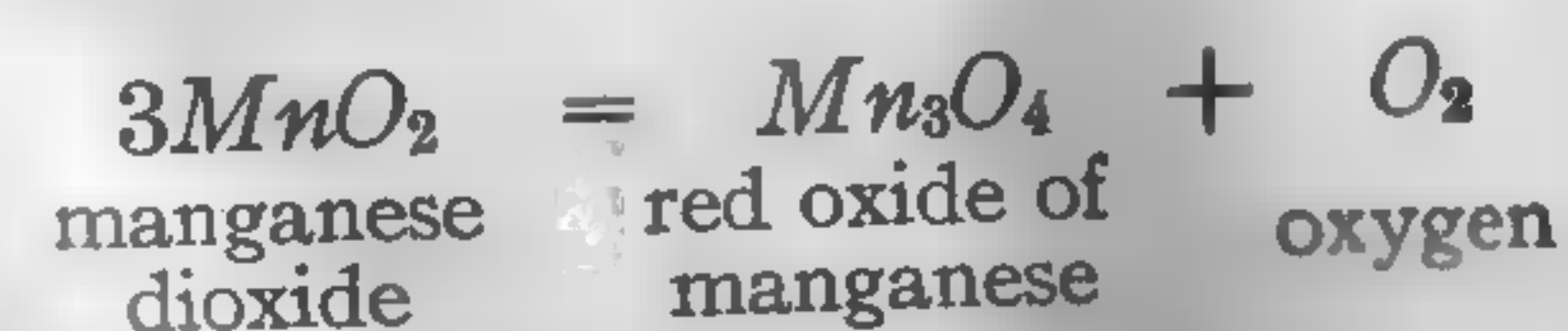


FIG. 9

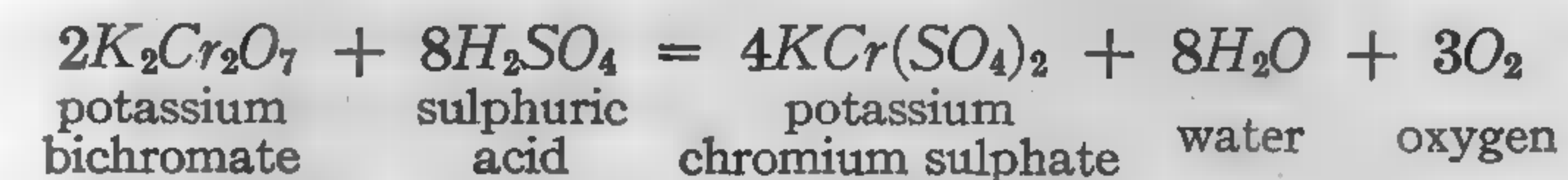
The oxygen absorbed is now disengaged, and the barium dioxide is converted into monoxide ready to absorb more oxygen.*

To make quantities of oxygen suitable for filling the gas holders of the laboratories of colleges and universities, the mixture of potassium chlorate and manganese dioxide is heated in a sheet-iron or copper retort, Fig. 9. At a bright redness manganese dioxide gives up one-third of its oxygen and is converted into red oxide of manganese.

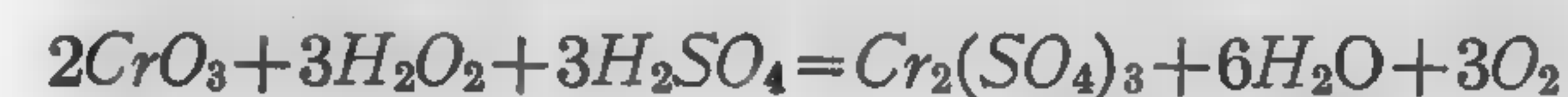


* Oxygen is now sold in New York, and other large cities, in strong steel bottles, from which it may be conveniently drawn as required for experiments.

Powdered potassium bichromate may also be heated with twice its weight of concentrated sulphuric acid, oxygen being disengaged.



Oxygen may be conveniently prepared without heating by the action of sulphuric acid and hydrogen peroxide on potassium bichromate. 150 grams of concentrated sulphuric acid and 1 liter of a commercial solution of hydrogen peroxide are gradually added to large crystals of potassium bichromate, in an apparatus similar to that used for the preparation of hydrogen sulphide. If a Kipp apparatus is used, small pieces of pumice must be placed beneath the potassium bichromate. Chromium trioxide is first formed by the action of the sulphuric acid on the bichromate, and this, in the presence of the acid, is decomposed by the hydrogen peroxide.



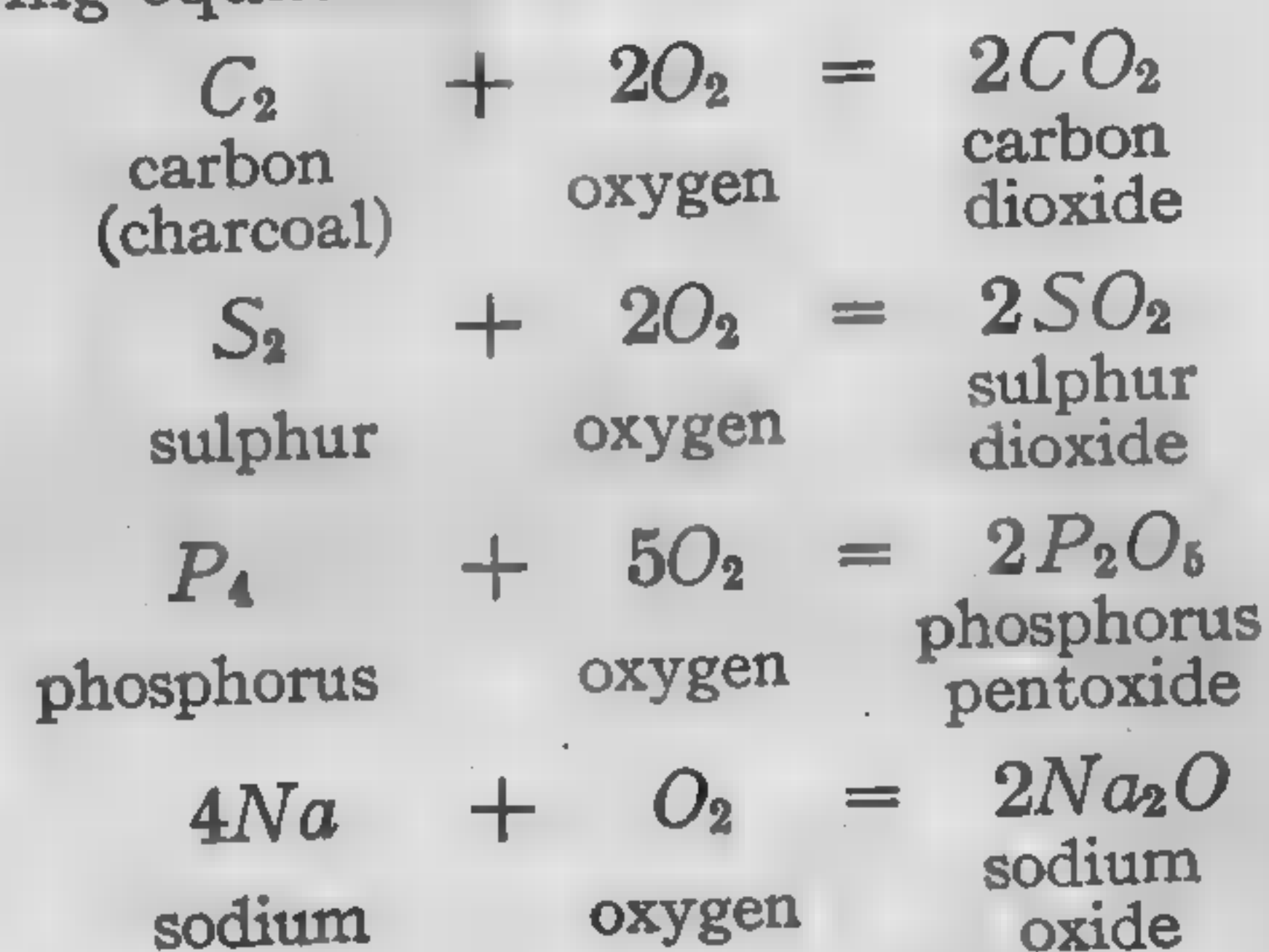
Oxygen is also prepared by the electrolysis of water.

14. **Properties.**—Oxygen is an odorless, colorless, and tasteless gas that is somewhat heavier than air, its specific gravity being 1.1056. It is slightly soluble in water, 100 volumes of water at 15° C. dissolving about 3 volumes of oxygen, and is magnetic; calling the magnetism of iron 1,000,000; that of oxygen is 377; hence, the magnetic power of atmospheric oxygen is quite appreciable. The diurnal variations of the magnetic needle are due, at least partly, to variations in the intensity of this magnetism, owing to the changes of temperature. Among its properties, by far the most important is that it possesses the power of supporting respiration. Oxygen in the pure state, however, is too active, so that a diluting agent is required; in the atmosphere this is supplied by the presence of nitrogen in large quantities. It also supports the combustion of inflammable bodies, though not itself inflammable. All substances that burn in the air burn with increased vigor and brilliancy in oxygen. Oxygen can be liquefied—its critical

temperature being -119°C . and its critical pressure 58 atmospheres. Liquid oxygen has a pale blue color, a specific gravity of 1.1181 at its boiling point of -182.5°C . Cooled with liquid hydrogen, it forms a pale blue solid mass melting below -223°C ., with a specific gravity of 1.4256 at -252.5°C .

When in a molten state silver and certain other metals absorb oxygen, which they give off on solidifying.

Oxygen enters into combination with all elements except fluorine and members of the helium group, and not directly with chlorine and bromine; but, as a rule, heat is necessary to accomplish this union. The class of bodies thus formed is an important one, to which the name of *oxides* has been given. The preceding experiments show the formation of several of these. The composition of the bodies produced is expressed in the following equations:



There is one important point of distinction between various oxides to which the student's attention will have been directed in the experiments performed: one group, of which sulphur dioxide is a representative, reddens a solution of litmus; another series, represented by sodium oxide, is characterized by the property of restoring the blue color to a litmus solution that has been previously reddened by an acid. The oxides of the first group, when dissolved in water, produce *acids*; those of the second group are known as *bases*.

15. Uses and Manufacture.—Oxygen is used in the arts for increasing the intensity of combustion, for purposes of either light or heat.

In the natural world, the uses of oxygen are nearly infinite. Diluted with nitrogen in the air, it is continually entering into and issuing from chemical combinations, setting free in the former, and absorbing in the latter, enormous stores of energy. It is by the oxygen of respiration that the energy of living beings is set free from their food; it is, again, by the separation of oxygen by the sunlight that energy is stored up anew in the food. It has been calculated that 6,000,000,000 pounds of oxygen are daily consumed in the respiration of living beings, and that the daily consumption of oxygen, for all purposes, reaches the incredible sum of 7,142,857 tons. There is, however, little cause to fear an exhaustion of the supply, since the air of the globe, even if no oxygen were daily added, contains sufficient of this gas to supply the enormous demand for, approximately, 480,000 years.

Various methods have been proposed for its manufacture. The most efficient of these are:

1. **Tessie du Motay's**, which consists, first, in passing pure air over a heated mixture of manganese dioxide and sodium hydroxide, producing, by its oxygen, sodium manganate; and, second, in heating this manganate still higher, by which, with the aid of a current of steam, it is decomposed into the original materials again, setting the oxygen free.
2. **Dewille's**, which consists in the decomposition of sulphuric acid by heat.
3. **Brin's**, which has been previously described.

OZONE

Allotropic oxygen. Formula O₃. Molecular weight 48. Density 24.

16. History.—The repeated discharges of an electric machine develop a peculiar odor, which is due to the production of a body that was discovered by von Marum in 1785. It was not, however, until 1840 that any searching investigations were made upon this subject. Then Schönbein noticed the similarity between this electrical odor and

that produced in the electrolysis of water, and showed that, in both cases, the substance produced turned paper, moistened with a solution of potassium iodide and starch, to a deep-blue color. In the same year Marignac and De La Rive proved this substance to be a modification of oxygen. In 1852, Becquerel and Fremy discovered a process by which pure oxygen could be converted into *ozone*. In 1860, Andrews and Tait showed that a contraction of volume occurred when oxygen became ozone, which means that 3 atoms of oxygen, in forming 1 molecule of ozone, occupies the same volume as 1 molecule of oxygen composed of 2 atoms; and, in the same year, Soret showed that oil of turpentine possessed the property of absorbing the entire molecule of ozone.

17. Preparation.—Ozone is produced by the passage of a series of electric sparks through either air or oxygen, and may be recognized by its peculiar odor, which can be observed whenever an electric machine is worked. The quantity of ozone thus obtained is, however, very small; but if a silent electric discharge is passed through the gas, care being taken to avoid sparks, a much larger proportion of oxygen will undergo this transformation. In order to effect this, arrangements are made so that the discharge occurs between large surfaces placed very near each other.

EXPERIMENT.—To perform this experiment a special apparatus is required. It consists of a thin, white glass tubing *ab*, as shown in Fig. 10 (a), which is closed at the bottom, except that a long piece of small-bore glass tubing *cde* is sealed into it at *c*, this tube being bent over in the shape shown in the figure. Inside the tube *ab* is fixed another one of smaller size *fg*, open at the top, but closed at the bottom similar to a test tube. These tubes are sealed to each other by fusion of the glass at *h*; immediately below this joint a side quill glass tube carrying a stop-cock *i* is fused into the outer tube. Between the tubes *ab* and *fg* there is, consequently, an annular space. If air is admitted at *i*, it traverses this space, and afterwards makes its exit through the tube *cde*. This constitutes the ozone-producing apparatus proper; in (b) it is shown fixed in an outer jar, and provided with other fittings in order to provide means for passing an electric current from the surface of *ab* to that of *fg* across the intervening annular space and through any gas contained in this space. The ozone tube proper is simply drawn separately in (a) in order that its construction may be more readily understood.

In (b), the tube *fg* is fitted with a cover *j*, to which is attached a binding screw *k*, and a platinum wire and sheet of platinum foil *lm* (electrode). The whole tube *ab* and inner limb *cd* of the small tube are contained within the outer glass jar *no*, being held in their place by the cover *pq*. Through this cover passes a binding screw *r*, carrying also a platinum electrode *st*. To use the apparatus, fill the outer jar *no* nearly to the top with dilute sulphuric acid (1 to 10), and also fill the inner tube *fg* to the same level with the same liquid. To the binding screws *k* and *r* attach copper wires leading from the terminal of a powerful induction coil. In

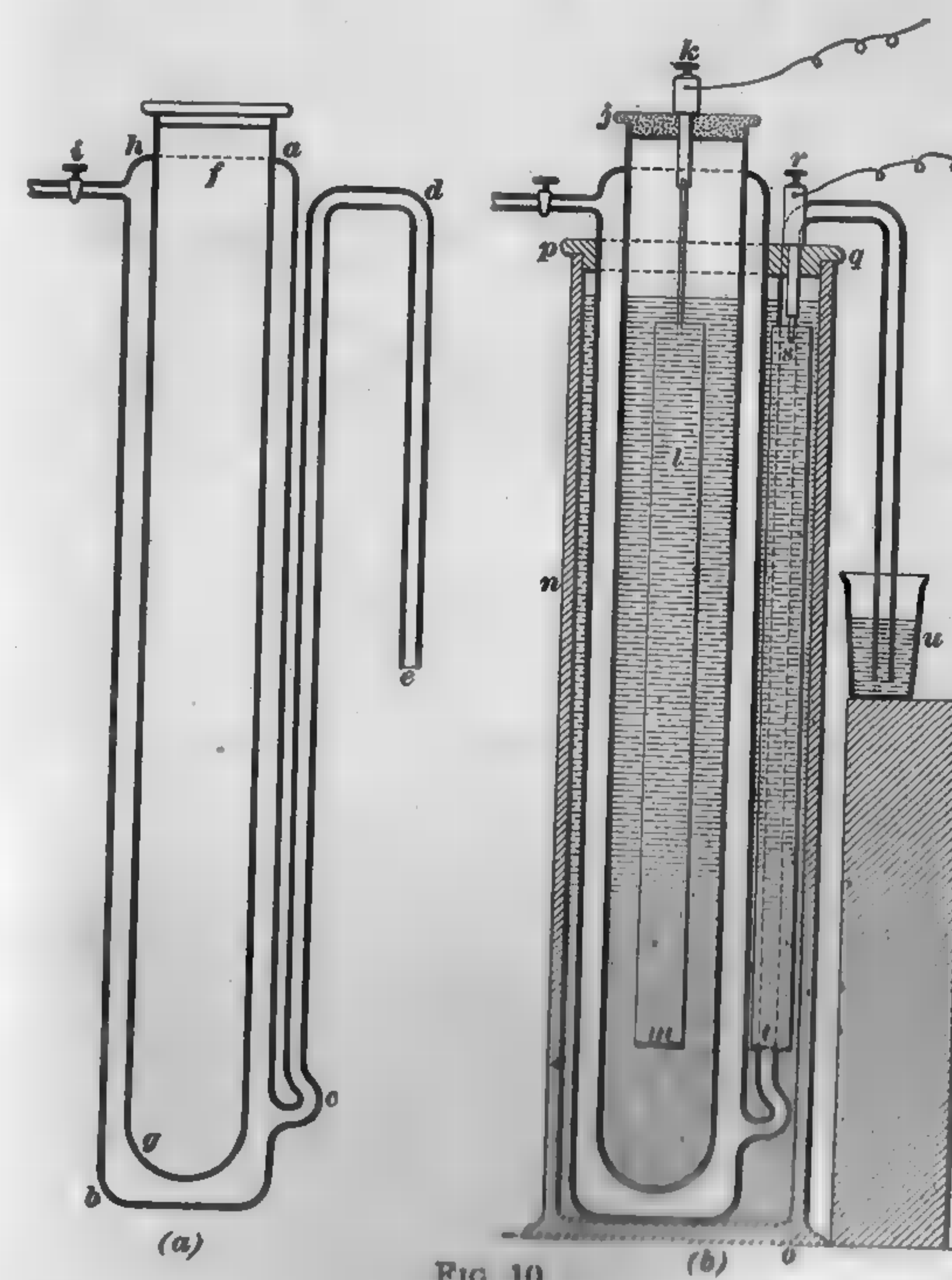


FIG. 10

turning on the electric current, it is conducted by means of the electrodes to the dilute sulphuric acid, which again conducts it to the surfaces of the tubes *ab* and *fg* arranged within each other; it then passes across the ring-like space as a silent discharge.

Having the apparatus so far in readiness, support a small beaker *u* containing water so as to receive the end *e* of the exit tube. Open the stop-cock *i*, and pass dry oxygen into the apparatus until it has displaced the air from the annular space between the tubes. (For this purpose, a volume of oxygen, about 4 or 5 times that of the annular space, should

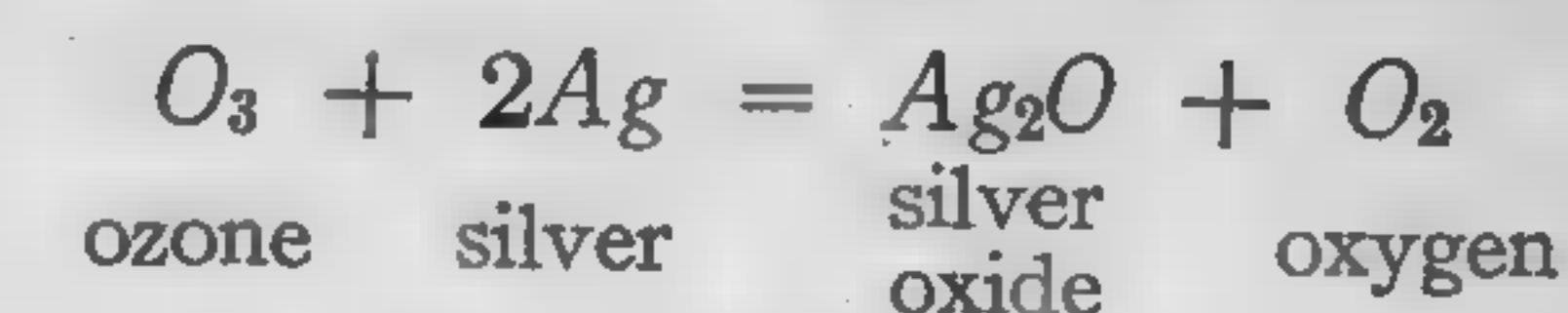
be passed through the tube.) Next close the stop-cock *i*, and observe that the tube *d e* is full of gas. Turn on the electric current from the induction coil through the apparatus; ozone is gradually formed, and the water rises in the tube *d e*, showing that the volume of the gas within is diminishing.

Having noted the diminution of volume, remove the beaker *u* and replace it by a small glass jar arranged for collection by downward displacement. Pass a slow current of oxygen through the stop-cock *i*, and collect the emergent gas in the gas jar. Under most favorable circumstances, however, the quantity of ozone produced by the transformation of oxygen does not amount to more than about one-sixth of the outflowing gas.

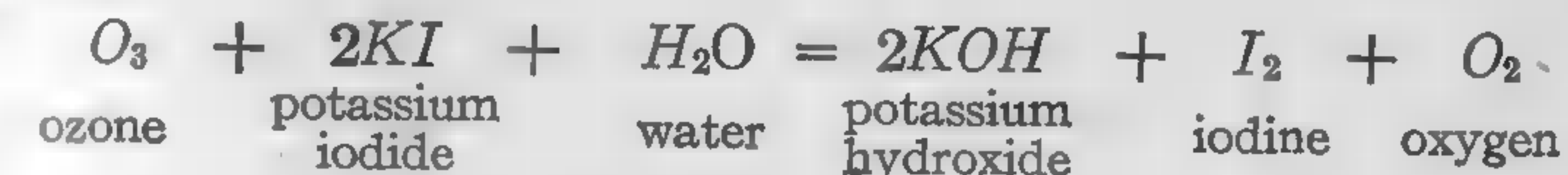
18. Properties.—Physically, ozone closely resembles oxygen, except in its density, which is just 1.5 times that of oxygen. It is allotropic oxygen. Chemically, it also resembles oxygen, as all its compounds are oxides. In fact, it is oxygen with properties intensified, and may be termed *active oxygen*. It possesses a peculiar odor, sometimes described as resembling that of weak chlorine. Hautefeuille and Chappuis have liquefied it by allowing the strongly compressed gas to expand suddenly; the liquid thus obtained boils at $-119^{\circ}\text{C}.$, is sky blue in color, the same as the compressed gas, the blue tint becoming more intense as the temperature is lowered or the pressure increased. At a temperature of $290^{\circ}\text{C}.$, it is reconverted into ordinary oxygen. On standing for some time it gradually changes into oxygen. The presence of water, however, retards this change to a very marked degree. Heat destroys ozone at once. Its most remarkable property is its energetic oxidizing power. Many of the metals, including even those so difficult to oxidize as copper, mercury, and silver, are rapidly converted into oxides by ozone. One of its most characteristic effects is that on mercury this reaction is so delicate that a very small bubble of oxygen containing only $\frac{1}{10}$ of its bulk of ozone will destroy the luster of several pounds of mercury and cause the mercury to lose its mobility and the convexity of its surface. Some non-metals are at once oxidized by moist ozone. For example, phosphorous is oxidized to phosphoric acid, sulphur to sulphuric acid, sulphides to sulphates, and ferrocyanides to ferricyanides.

During oxidation by ozone no diminution of the volume of the gas occurs; it is, in fact, the extra volume of oxygen

that enters into combination, the normal oxygen set free occupying the same space as the original ozone. This fact is represented in the following equation:



Ozone bleaches strongly, and is poisonous to animal life on account of its irritating effects on the mucous surfaces. It is soluble in oil of turpentine and slightly soluble in water. The oxidizing power of ozone leads it to immediately decompose potassium iodide when the two are brought into contact, in a neutral solution, the potassium being oxidized and the iodine set free.



19. Tests.—*Schönbein's test* is based on the property of ozone to immediately decompose any potassium iodide that is brought into contact with it. It consists of paper moistened with a dilute solution of potassium iodide and starch; the iodine is set free by the ozone and colors the starch deep blue.

EXPERIMENT.—To prepare Schönbein's test paper, put a piece of starch, the size of a large shot, into a test tube and add some water; shake up thoroughly and boil over the Bunsen burner; add a piece of about the same size of potassium iodide, and allow it to dissolve. Dip some pieces of filter paper in the solution, and introduce one of these pieces into a jar filled with ozone. A blue tint is immediately produced on the paper.

Fremy's test is paper moistened with an alcoholic solution of guaiacum; it is turned to a light-blue color by ozone. Paper moistened with manganous sulphate or lead hydrate becomes dark brown or black in ozone.

As ozone, nitrogen peroxide, and hydrogen peroxide all have the common property of liberating iodine from potassium iodide solutions, the presence of ozone in a mixture of these substances can be detected by passing it through a solution of potassium permanganate, which destroys the peroxides of nitrogen and hydrogen.

20. Occurrence.—Ozone probably occurs free in the atmosphere that surrounds us after electrical disturbances, and its odor is sometimes apparently noticeable after thunderstorms with violent electric discharges. It is also produced by the decay of animal and vegetable matter and thought by some to be by the growth of plants. It was formerly thought that ozone was a normal constituent of the atmosphere, but at present this seems very doubtful. One of its chief functions in nature is to oxidize, and thus destroy impurities in the air. Atmospheric ozone burns up miasmatic exhalations, and in this way preserves a natural state of purity in the air.

21. Uses.—Ozone has found utility in the arts as a bleaching agent and as a disinfectant.

22. Summary.—Oxygen occurs plentifully in nature and is widely distributed. It was discovered in 1774 by Priestley. It may be prepared by the decomposition of mercuric oxide, potassium chlorate, or manganese dioxide. Remember that manganese dioxide assists the decomposition of potassium chlorate without itself undergoing any noticeable change. Oxygen forms compounds called oxides, one group of which reddens litmus paper. Another class restores the blue color to the litmus paper thus reddened. It is a colorless, odorless, and tasteless gas, supporting respiration and combustion, but is not inflammable by itself. Alone it is neutral to litmus in its action.

Ozone is a condensed form of oxygen, possessing a peculiar odor, sometimes compared to that of chlorine. It is produced by the passage of electricity through air. It is much more active than oxygen.

23. Object Demonstration.—Observe the appearance and general characteristics of the following: Potassium chlorate, a colorless salt occurring in tabular or flat crystals; manganese dioxide, a heavy, black powder, produced by grinding the natural form of the substance; iron oxide, which is produced by the combustion of iron in oxygen, consists of brittle molten globules.

Study carefully the apparatus and general arrangements for the production of ozone (Art. 17 and Fig. 10).

Starch is a white powder that dissolves, on heating, to a pasty liquid. Potassium iodide is a white salt, occurring in cubic crystals.

24. Laboratory Directions.—In Arts. 11, 17, and 19, a number of very important and instructive experiments have been described. Experiments 1, 3, and 4, Art. 12, are generally confined to the lecture table, and the performance of the others must be left to the discretion of the student. Note, however, in each case, the general arrangement of the apparatus, and the general lesson each experiment is intended to convey. Experiments 1 and 3, Art. 11, and 1 and 3, Art. 12, should, however, if possible, be performed by the student.

For the generating apparatus, Fig. 6, take a test tube $\frac{5}{8}$ inch in diameter and 5 inches long. Select a stopper that just fits it. Take a piece of glass tubing, about 18 inches long, and bend it to the shape shown in Fig. 11, and round off the edges.

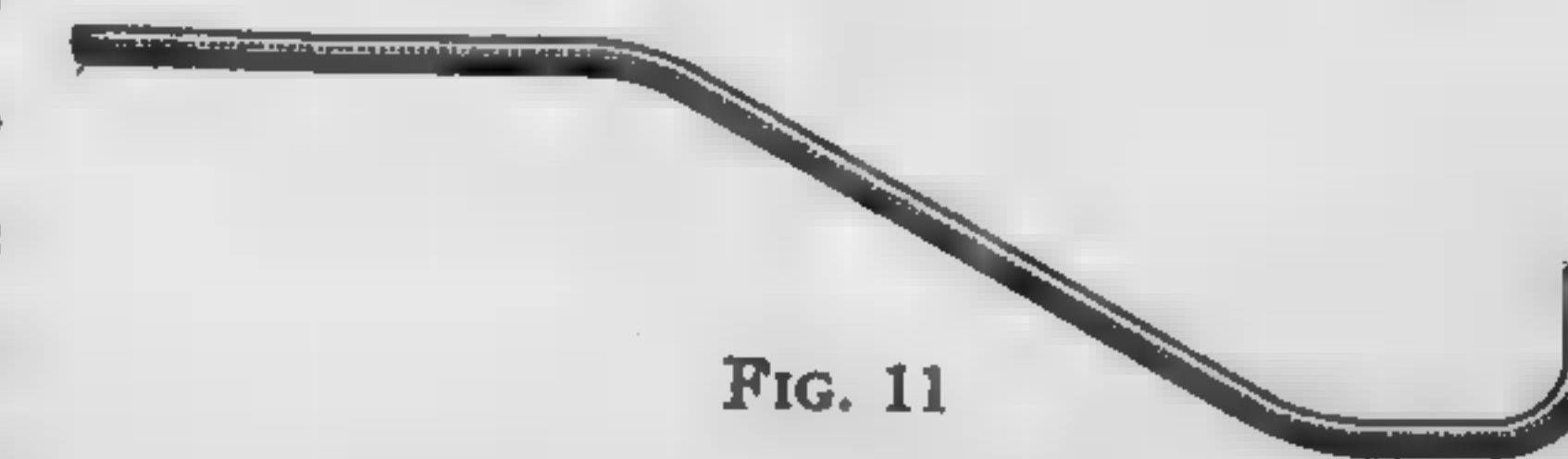


FIG. 11

If a cork stopper is used, it will be necessary to bore a hole in it. For this purpose an instrument called a *corkborer* is used; it consists of a set of several thin, brass tubes, the lower ends of which are sharpened. A rod is also contained in the set, in order to thrust out of the borer the pieces of cork cut from the holes. The rod can also be pushed through two holes in the top of the borer, forming a handle to grasp when boring. Before commencing to bore, see that the borer is clear; then, beginning at the small end of the cork, bore carefully by twisting the borer and pushing it through. Take care, while this is going on, that the hole is perfectly straight. Do not place the cork against a table or bench and bore into the wood, as this will blunt the borer and diminish its usefulness. The hole should be cut, not bruised, through. The borer selected should be just a trifle less in diameter than the glass tubing you are going to use. This will tend to produce an air-

tight fitting. It will be found of advantage to rub a little grease on the glass tube, in order to facilitate its passage through the hole of the cork. While attempting to force the glass tube into this hole, cover your hand with a cloth as a protection in case the tube should break. Remember that the success of your experiments depends, to a large degree, on the fact that the stopper, as well as the glass tube, fits perfectly air-tight. Much time and trouble is saved by fixing up every piece of apparatus as nearly perfect as possible.

On account of the difficulty in getting cork stoppers to fit air-tight, rubber stoppers are nearly always used in fitting up chemical apparatus.

In the special sketches, subsequently given, the student may often adopt bent glass tubes already made by the use of rubber connections, instead of making new ones of the exact shape shown.

The terms *leading tube* and *delivery tube* are applied to the tube by which a gas emerges from any particular piece of apparatus.

For experiments, gases are usually collected in *gas jars*. Any wide-mouthed pickle jar or milk bottle will answer this purpose; they should, however, be made of white glass.

The gas is most easily retained in any bottle by placing a ground-glass plate on the mouth, which should be ground flat. This is very quickly and easily done, thus: Take a piece of ordinary plate glass; place on it some emery of medium coarseness, and moisten it with water; then take the bottle, hold it firmly, mouth downwards, on the plate, and rub in a circular motion. A minute's rubbing will generally be sufficient to grind the top true. The joint between the glass plate and the bottle is rendered air-tight by smearing the glass plate with a little grease. Resin cerate, which is obtainable in every drug-gist's store, may be recommended for this purpose; petrolatum or vasoline is also very good.

25. Gases that are only slightly soluble or entirely insoluble in water are, as a rule, collected over the pneumatic trough filled with water; this process is known as *upward displacement*

of water. Gases that are soluble in water are collected either over the pneumatic trough filled with mercury, or, more conveniently, by the process of *displacement of air*.

In this operation the gas pours into the bottle and drives the air out. If the gas is heavier than the air, stand the bottle upright, and let the delivery tube from the generating apparatus reach to the bottom of the bottle, thus collecting the gas by *downward displacement*. After the bottle is filled, cover it with a piece of glass or cardboard, in order to prevent the escape of the gas by diffusion. In order to find out whether the bottle is entirely filled with the gas, test from time to time near its mouth. The test employed, of course, depends entirely on the nature of the gas; oxygen, as has been already stated, for instance, may be recognized by its property of igniting a glowing spark.

Should the gas be lighter than the air, the whole arrangement must then be inverted; the gas is then said to be collected by *upward displacement*. This may be either over water, as in the case of oxygen, or may displace the air. The vessel, when air is displaced, is inverted over the tube conveying the gas from the vessel in which it is generated and the gas passes upwards to the bottom of the receiving vessel and drives the air downwards and out at its mouth.

COMPOUNDS OF OXYGEN WITH HYDROGEN

WATER

Formula H_2O . Molecular weight 18.016. Density 9.008. Specific gravity 1. Solidifies at $0^\circ C$. Boils at $100^\circ C$.

26. History.—Until 1776 water was considered an element, when Lavoisier proved its compound nature. Cavendish and Watt, in 1781, proved its composition by synthesis, and in 1805 Humboldt and Gay-Lussac ascertained the ratio of its constituents by volume to be 1 : 2, while Berzelius and Dulong succeeded in proving its combining ratio by weight to be 1 : 8.

27. Occurrence.—Water, either free or combined, occurs most abundantly in nature. Natural waters are, however, rarely pure, owing to their great solvent power, and even rain water is more or less contaminated. It is well known that water is an essential to animal and vegetable life. Seven-eighths of the entire human body is water.

28. Preparation.—Water occurs so plentifully in nature that, except when required for chemical purposes, no special process of preparation is necessary. Chemically pure water is obtained by freeing the natural water from the foreign substances it usually contains, and, as most of these are solids in a state of solution, the water is purified by the *process of distillation*.

29. Properties.—Between the temperatures of 0° C. and 100° C., water is a tasteless, limpid liquid, and when viewed in a moderate quantity is colorless. When seen in large masses it shows a distinct greenish-blue tint. It is neither acid nor alkaline in its action on vegetable colors; it is a poor conductor of heat and when perfectly pure is a non-conductor of electricity. It is almost incompressible, losing only 50 volumes in 1,000,000 volumes when the atmospheric pressure is doubled. Its most important property is its solvent power; there exist comparatively few substances that it does not dissolve in larger or smaller quantities. The oceans are the natural reservoirs from which our water supplies are drawn. By the heat of the sun, immense quantities of sea-water are converted into vapor, which either remains suspended in the air or condenses to produce clouds. Special atmospheric conditions lead to the precipitation of this moisture as rain or snow. Rain and snow are the direct or indirect sources of spring and river water; these latter always contain more or less solid matter, depending on the condition of rock and soil over or through which they have been passing. The rivers always carry down with them a certain proportion of solid matter to the ocean, which precipitates when the water is again vaporized to form clouds. In this way occurs a continuous, though slow, increase in the quantity of matter found in sea-water, which, as a result, has its well-known saline

taste. The constitution of sea-water naturally varies to a certain extent, according to locality and climate, but its principal constituents always are sodium chloride, magnesium compounds, and a number of other salts, of which iodine and bromine are the most important.

EXPERIMENT.—Evaporate to dryness on a clean piece of platinum foil a few drops of water; notice that a perceptible residue remains; repeat the same experiment with a few drops of distilled water, and compare the results.

30. Natural Waters.—Water is never met in an entirely pure state in nature, as has been previously stated. Whether it has rested on, or has flowed over, the surface of the soil; whether it has fallen in the form of dew, mist, or rain, or whether it has just emerged from its subterranean passages, it always contains more or less solid matter in a state of suspension or of solution. The purest form of natural water is rainwater. Other natural waters may be divided into *potable*, or *drinkable*, *mineral*, and *saline waters*.

River and lake waters, especially such as are found in granite regions, are, as a rule, the purest. The water of Lock Katrine, in Scotland, for instance, does not contain more than 2 grains of solid matter to the gallon, and is one of the purest natural waters known. The following are the amounts of impurity in the water supplies of some of the large cities: That from Lake Cochituate, which furnishes the city of Boston with its water supply, contains only 3.11 grains of impurities to the gallon; the Schuylkill water, which supplies Philadelphia, contains 7.78 grains; the waters collected in the reservoirs of Ridgewood, for the supply of Brooklyn, 3.92 grains; the Croton water of New York City, 4.78; Lake Michigan, from which Chicago draws its water supply, 6.68 grains in every gallon. The water of the Thames, which, to a great extent, supplies London, contains nearly 10.68 grains of impurities to each gallon.

Spring and well water, owing to the fact that they have, previous to their issue, penetrated the soil, are never as pure as surface waters. Thus, the water of a well near Central Park, New York City, gave 43.54 grains; one in Schenectady,

49.21 grains; one in Amsterdam, Holland, 69.93 grains; and one in London, England, 99.97 grains of solid matter to the gallon.

Mineral and saline waters are those which, by virtue of their chemical constituents or temperature, have a certain effect on the animal economy, and hence possess a therapeutic (medicinal) value.

They are either cold or warm; they are termed warm when they possess, at the moment of their issue, a temperature above 15° C. Their thermal state, of course, varies, covering the whole range of the thermometer from 15° C. to 100° C. There are numerous hot springs in Virginia, Colorado, and California. The temperature of the Grand Geyser, in Iceland, is far above 100° C.

31. According to their chemical constituents, mineral waters are classified in a number of characteristic groups, distinguished either by the predomination of certain constituents or by the presence of certain distinctly active components. These waters may be distinguished as follows:

Acidulous, or gaseous, waters, characterized by the presence of free carbon dioxide.

Alkaline waters, characterized by the presence of a larger or smaller proportion of sodium bicarbonate, or of an alkaline silicate, as well as common salt, and Glauber salt.

Chalybeate waters, characterized by holding an iron salt in solution.

Saline waters, or those which contain neutral salts, replacing the alkali bicarbonate.

Sulphur waters, characterized by the presence of hydrogen sulphide and other soluble sulphides.

Acidulous, or gaseous, waters are distinguished by the presence of free carbon dioxide, which is dissolved in the depth of the earth and under a pressure much greater than that of the atmosphere; hence, a certain portion of this gas becomes naturally disengaged as soon as the water emerges from the soil, thus creating more or less effervescence. Gaseous waters are cool, and their taste is pleasant at the moment of issue, but

sometimes these waters become saline, or even alkaline, after the disengagement of the greater proportion of their carbon dioxide. Natural gaseous waters never consist of a solution of carbon dioxide in pure water; they always contain a certain quantity of saline matters, such as sodium, calcium, and magnesium carbonates, and sometimes even traces of chlorides and sulphates. Such is approximately the composition of certain of the *Saratoga springs*, and the well-known *Seltzer water*.

Alkaline waters, as their name indicates, possess an alkaline reaction. This alkaline reaction is sometimes noticed immediately on their emergency, sometimes only after the loss of their free carbon dioxide. This reaction may be due to an alkaline silicate, but can generally be referred to an alkaline carbonate. Acid sodium carbonate, or sodium bicarbonate, HNaCO_3 , popularly known as *bicarbonate of soda*, is present in nearly all waters of this class. *Vichy water*, for instance, contains nearly 5 grams of this salt per liter.

Chalybeate waters are distinguished by holding more or less iron in solution, which gives to these waters an astringent taste and certain therapeutic properties. The traces of iron they contain may exist in three conditions: (1) As ferrous carbonate held in solution by carbonic acid. (2) As ferrous crenate. Berzelius gave the name of crenic acid to a body that is related to peculiar acids existing in the soil, and which are known as ulmic, humic, and geic acids. Ferrous crenate is soluble in water; its constitution, however, is at present unknown. (3) As ferrous sulphate. Hence, chalybeate waters may be carbonated, crenated, or sulphated.

Such waters, however, seldom contain ferrous salts in really considerable proportions; in fact, many ferruginous waters (that is, waters containing ferrous salts) of undoubted sanative power do not contain more than about 4 centigrams of these salts per liter. Through exposure to air they lose the greater portion of their carbon dioxide very soon, and ferrous carbonate is precipitated, which, in turn, soon loses its carbon dioxide and is converted into brown ferric hydrate. Springs of chalybeate water frequently occur in this country as well as in Europe. They exist in Bedford, Pennsylvania; Manitou, Colorado; Sara-

toga, New York; and many other places. The springs of Spz and Pyrmont, in Belgium; Bussang, in the Vosges; and Passy, near Paris, are known all the world over.

Saline water includes a great number of waters of various composition, charged with neutral salts, among which the most prominent are the chlorides, bromides, and iodides. According to the predominating or most active constituent, they are classified as chlorinated, sulphated, and bromo-iodated waters.

Sea-water is a chlorinated water. It is a well-known fact that it contains a notable proportion of sodium chloride. This common salt is accompanied by the chlorides of potassium and magnesium and by a considerable amount of magnesium sulphate.

Sulphur water contains a soluble sulphide or hydrogen sulphide. This class of waters is divided into two distinct classes, namely, *natural sulphur waters* and *accidental sulphur waters*. The first class contains sodium sulphide, is hot when emerging from the soil, and contains little solid matter. The second class of waters embraces those that are formed on the spot by the reduction of sulphates, and particularly calcium sulphate, contained in the waters. This reduction is accomplished by the action of organic matters that impregnate the soil, and of which the combustible elements, carbon and hydrogen, remove the oxygen of the sulphates.

32. Effects of Heat on Water.—Among other properties of water, the physical changes it undergoes as a direct result of the application of heat are of such vast importance as to justify a somewhat extended description. It is a well-known fact that, at a temperature below the freezing point, water exists in the solid state. Every one is familiar with ice. Taking a piece of ice at a temperature considerably below that at which it was formed, say -20°C. , the following is a description of its changes as a result of the continuous application of heat:

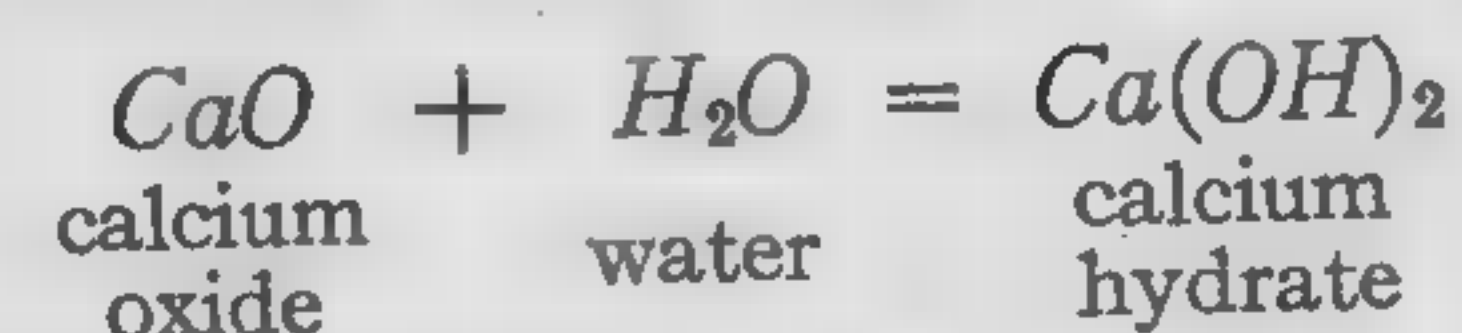
As heat is first applied, the ice rises in temperature and at the same time increases in volume (expands); these changes

proceed regularly until a temperature of 0°C. is attained. At that point the temperature remains stationary, notwithstanding the fact that the absorption of heat continues. During this time the ice melts, and the heat thus absorbed, without causing any corresponding elevation of temperature, is employed in converting the solid ice into liquid water. The heat necessary to melt a given quantity of ice at 0°C. into water at the same temperature would raise the same weight of water from 0°C. to 79°C. , a fact that is expressed in other words by saying that the latent heat of water is 79 heat units. During the melting of ice a considerable diminution of volume occurs, only 10 volumes of water being produced by 10.9 volumes of ice. As soon as the whole of the ice is melted, the temperature once more begins to rise, and does so steadily until a temperature of 100°C. is attained. The water at 0°C. diminishes in volume with an increase in temperature, until at 4°C. , when it commences to expand, and continues to do so until 100°C. is reached. At 4°C. , or more accurately 3.945°C. , therefore, water is at its maximum density; either a diminution or an increase of temperature will result in expansion. At 100°C. and the normal pressure of 760 mm. the water begins to boil and remains stationary in temperature, but is not all at once converted into vapor; on the contrary, between five and six times as long is necessary to boil away the whole of the water as was needed to raise it from the freezing to the boiling point. Or, to express it in exact figures, the quantity of heat, *the latent heat of steam*, necessary to convert a given weight of water into steam is sufficient to raise 536 times the same weight of water from 0°C. to 1°C. The steam produced is at the same temperature, 100°C. , as the boiling water; this large amount of heat is employed in the conversion of the water from the liquid to the gaseous state. The whole of the water having been converted into steam, a further application of heat results in the expansion of the steam, which follows the general laws governing the relation of gases to heat.

In cooling, steam passes through a series of changes that are just the converse to those that it experiences on being heated. During the condensation of steam into water, and

the solidification of water to form ice, heat is liberated in the same quantity as was required in the first place to effect, respectively, the liquefaction of ice and the conversion of water into steam.

33. Chemically, water is an active compound, entering into combination directly with most oxides, forming bases and acids, as the case may be, with the evolution of more or less heat. One of the most familiar examples of this is the slaking of lime, a process that may be represented by the following equation:



Water also enters molecularly into the composition of many crystalline substances, the amount appearing to increase in proportion as the crystallization takes place in a colder and more dilute solution. Calcium sulphate crystallized takes 2 molecules, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; copper sulphate, 5, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; sodium sulphate, 10, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; etc. If such crystals are exposed to dry air, they *effloresce*, which means that they lose their water of crystallization and fall into an opaque, white powder.

Other crystallized substances, again, in a moist temperature, attract water and liquefy, which is termed *deliquescence*. It has already been mentioned that the solvent power of water is greater than that of any other liquid known; but, of course, each substance soluble in water has a certain limit of solubility, this limit depending on such conditions as temperature, pressure, etc.

Gases, as a whole, are much less soluble in hot than in cold water.

34. Composition of Water by Volume.—It has been previously stated that, until within the last hundred years, water had been considered as an element. The experiments in Arts. 3 and 6 will have shown the student that its composition is compound, hydrogen having been obtained from it; and water, on the other hand, having been produced by the combustion of hydrogen in the atmospheric air.

By the application of intense heat, water may be separated into oxygen and hydrogen, but the difficulty met is that, as the gases cool down, they once more combine and reproduce water.

The most convenient source of the necessary heat to separate water into its constituents is the electric spark.

EXPERIMENT.—The necessary requirements to perform this experiment, which is mostly confined to the lecturer's table, consist of a piece of apparatus composed of a glass bulb *A*, Fig. 12, through which platinum

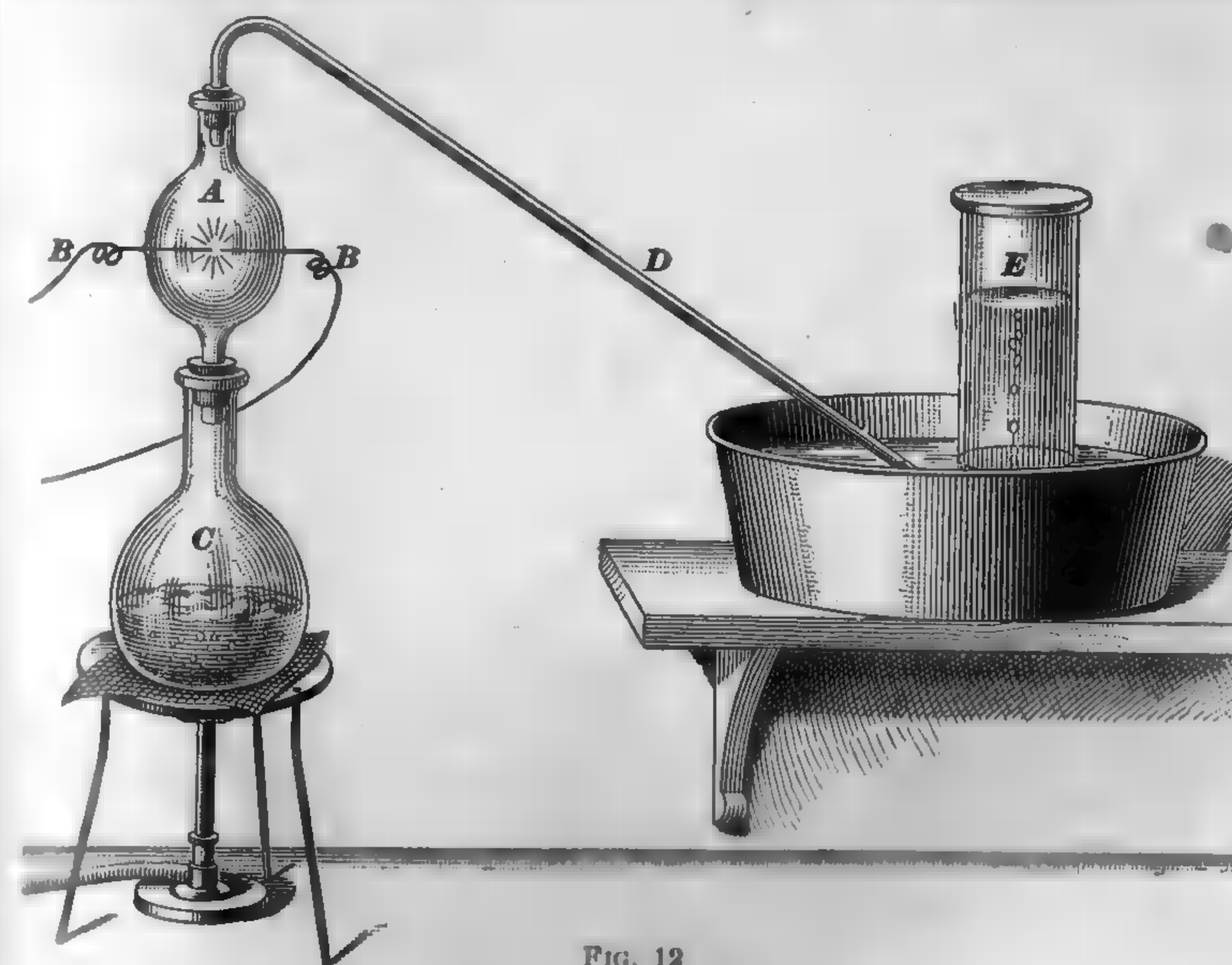


FIG. 12

wires *B, B* are so fixed that their ends are in the center of the bulb, and, approximately, $\frac{1}{8}$ inch apart. The lower part of this bulb *A* is provided with a glass tube, which passes through a stopper fitted into the mouth of a flask *C*. There is further fitted to bulb *A*, through a stopper, a leading tube *D* passing into a pneumatic trough for the collection of any evolved gases. After the flask *C* is filled about one-half with water and the approaches reconnected, the water in *C* is boiled until the arising steam has expelled the whole of the air from the apparatus, the steam itself being condensed by the cold water in the trough. At this stage a series of sparks from an induction coil is passed through the wires *B, B*, and a small gas jar *E* is arranged to collect any gas escaping from *D*. The passage of each spark decomposes a small quantity of steam, and, the mixed gases being

immediately largely diluted with steam, some proportion, at least, is kept apart until the gases have cooled below their combining temperature. In this way the gas jar is slowly filled with an explosive mixture of hydrogen and oxygen, the jar is removed, a light applied, and a violent explosion ensues.

35. The most convenient force to apply, for the purpose of the above-described decomposition, is undoubtedly that of voltaic electricity. The following experiments on the analysis of water by electricity (electrolysis), and its synthesis, should, as the average student will not be able to perform them himself, be read very carefully; the directions given, and the

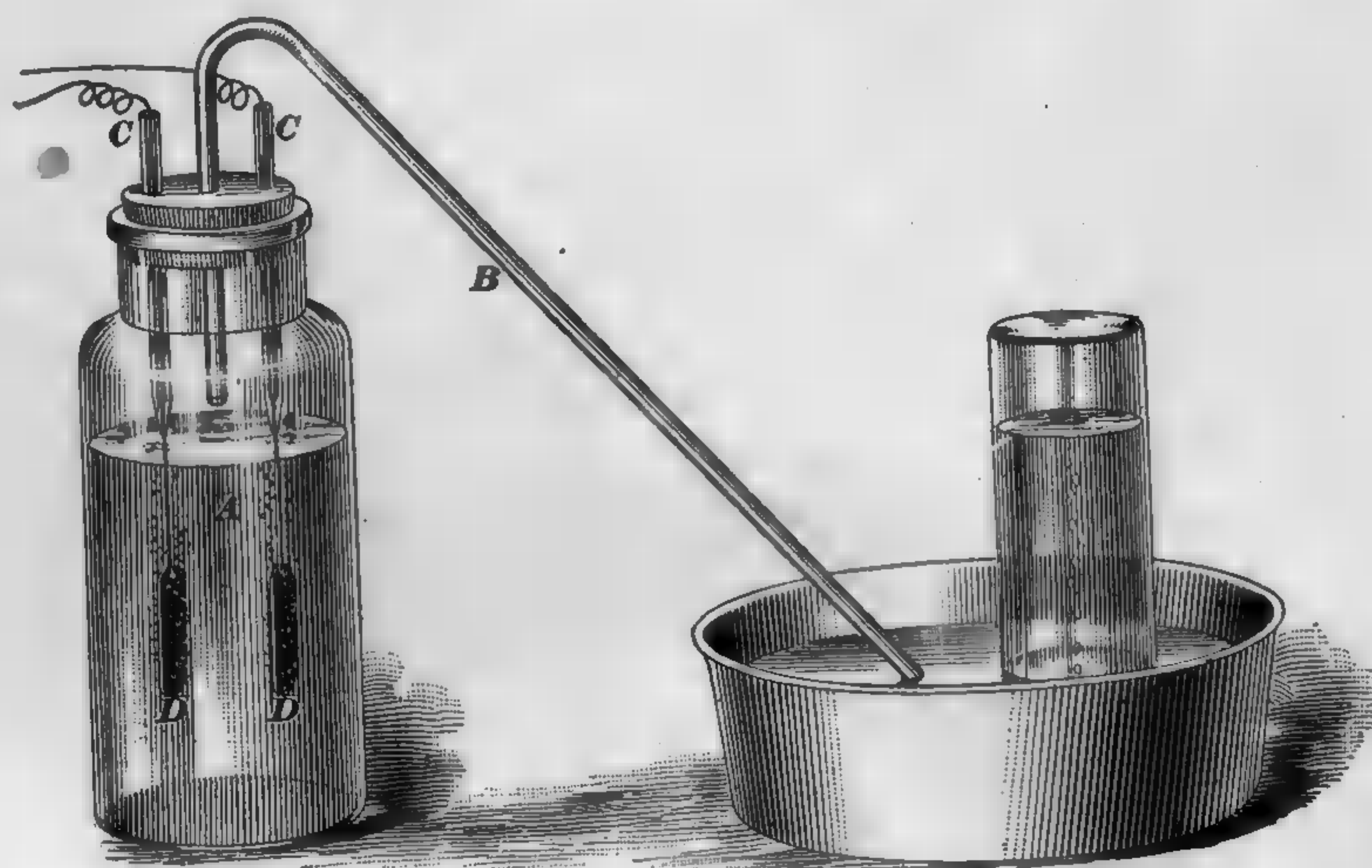


FIG. 13

general arrangement of the apparatus, as well as the results obtained, should be studied very carefully.

EXPERIMENT 1.—The electrolytic apparatus shown in Fig. 13 is to be attached by means of the wires to a battery consisting of two or three Bunsen cells. Such an apparatus is easily constructed by taking a wide-mouthed bottle *A*, Fig. 13, of about 8-ounces capacity, and fitting it with a good stopper, through which passes the delivery tube *B*, and the necessary appliances for conveying a current of electricity to the contained liquid. For this purpose a very convenient arrangement consists of the glass tube *C, C'*, as shown in the figure. Into the lower end of these are fused pieces of platinum wire, to which small pieces of platinum foil *D*

are attached. The tubes are then filled with mercury, and the connection with the battery is readily made by pushing the clean ends of the wires into the liquid metal.

In order to use the apparatus, the bottle is filled to the neck with water, to which between 25 and 30 drops of sulphuric acid has been previously added. Then the battery is connected, and we soon notice that a stream of bubbles of gas ascends from each piece of platinum. The gas issuing from the leading tube is collected in a bottle over the pneumatic trough. When entirely full, the mouth is closed with a stopper, the bottle is carefully wrapped up in a cloth, and after the stopper is again removed and a light applied, a violent explosion of the gas will take place.

Further information may be gained from a modified form of this experiment, in which the gas evolved from each of the electrodes is separately collected.

EXPERIMENT 2.—A typical form of apparatus for this purpose is shown in Fig. 14, which consists of a shallow glass basin *A*, containing water, to which a little sulphuric acid has been added (acidulated water), and two electrodes connected to the binding screws *B, B'*. The glass tubes *C, C'* are also filled with acidulated water, and

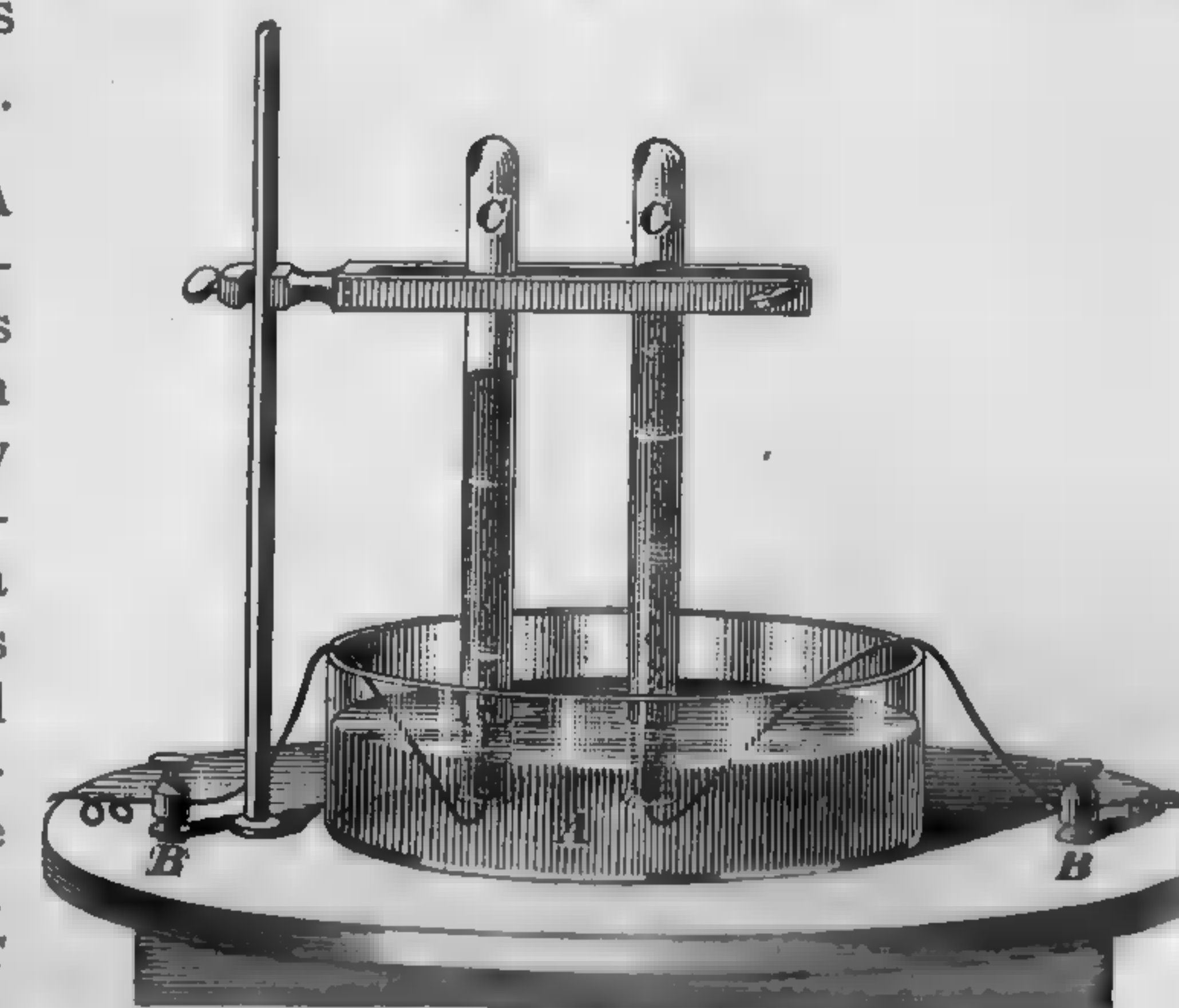


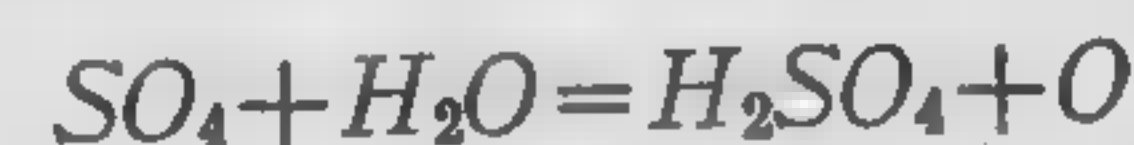
FIG. 14

each is inverted over one of the electrodes. The battery wires are connected to the binding screws *B, B'*, to which the electrodes have been attached. As soon as this connection has been made, it will be noticed that gas immediately begins to rise in each of the tubes, and it will soon be further noticed that in the tube inverted over the negative electrode the volume is double that evolved from the positive electrode. When the tube containing the larger quantity of gas, that is, the one over the negative electrode, is nearly full, it is removed, and a light applied to its mouth; the collected gas burns quietly, with the familiar blue flame of hydrogen. In the second tube of gas a glowing match is plunged, with the effect that it is instantaneously relighted, thus proving this gas to be oxygen.

These experiments, and especially the last one, prove that water may be decomposed into its components, viz., hydrogen

and oxygen, and, furthermore, that these components exist in water in the proportion of 2 to 1.

If pure water were used for electrolysis it would not conduct the current and consequently there would be no action; therefore, water containing some sulphuric acid must be used. It must be remembered, however, that the passage of the electric current does not directly decompose the water. The sulphuric acid present forms ions of hydrogen and SO_4 , the former giving up its electrical charge at the negative pole, while the SO_4 ions give up their charge at the positive pole, decompose at once, yielding oxygen, and form a fresh quantity of sulphuric acid, thus:



36. The student should also learn that the reunion of oxygen and hydrogen again produces water.

EXPERIMENT.—The gas jar used for the collection of the mixed gases in the electrolysis of water, described in Experiment 1, Art. 35, and shown in Fig. 13, is

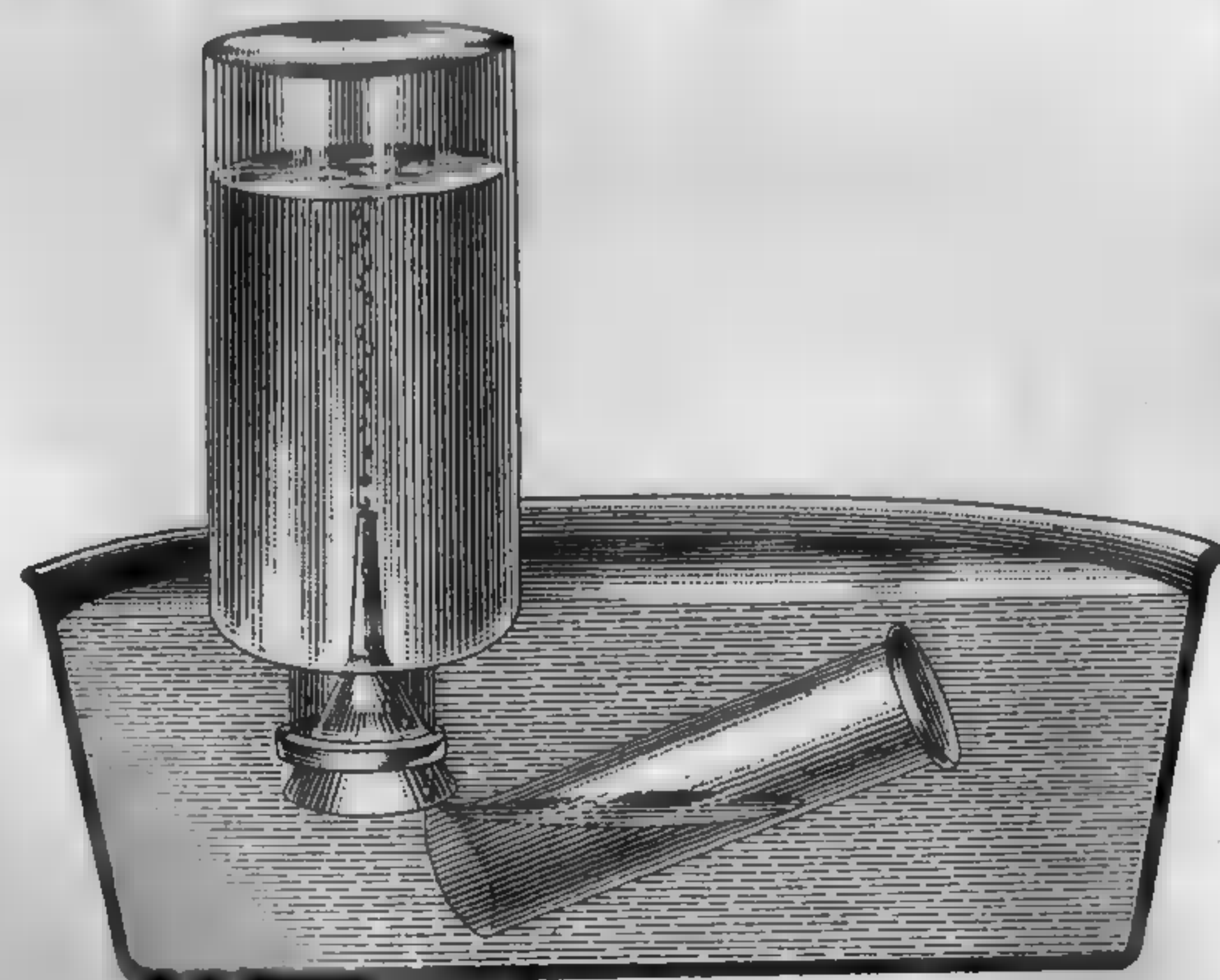


FIG. 15

filled with water, which is then poured out into a graduated measuring tube; one-third of its contents is poured back into the gas jar, and the height of the water in it is marked by a file scratch on the outside of the bottle; another third is added and again marked in a similar way. This bottle is then placed in the pneumatic trough filled with water, and from a jar, previously filled with oxygen, one-third of the original jar is filled with oxygen; this is done in the manner shown in Fig. 15. After that, the remaining two-thirds of the bottle is filled in the same way with hydrogen. After removing the bottle from the pneumatic trough, it is shaken up, so as to cause a thorough diffusion of the two gases, the bottle is securely wrapped in a cloth, in order to prevent injury to the hands in case of explosion, and a burning match applied

shown in Fig. 13, is filled with water, which is then poured out into a graduated measuring tube; one-third of its contents is poured back into the gas jar, and the height of the water in it is marked by a file scratch on the outside of the bottle; another third is added and again marked in a similar way. This bottle is then placed in the pneumatic trough filled

to the mouth of the bottle. It explodes in just the same manner as the detonating gas collected by electrolysis.

The recombination of hydrogen and oxygen may also be effected with the aid of the electric spark, which is passed through a mixture of these gases. Cavendish, in his investigations, made use of a strong glass vessel, with two platinum wires inserted in it, so that the electric spark might pass through the gases between their ends, as shown in Fig. 16. *A* represents the glass vessel, which, after being exhausted by an air pump, is attached to a graduated glass jar *B* containing a mixture of 2 volumes of hydrogen and 1 volume of oxygen. On opening the stop-cock *C* the vessel fills with the mixture of gases. The stop-cock is again closed, and an electric spark is flashed through this mixture; drops of water will be noticed to condense on the sides of the vessel. This operation may be repeated a number of times, until the whole of the gases have been caused to combine; by this time there will be an appreciable quantity of water in the glass vessel.



FIG. 16

37. For the purpose of measuring exactly the proportions in which hydrogen and oxygen unite, an instrument called a *eudiometer* is employed.

Fig. 17 represents a form of this apparatus, proposed by Ure. It consists simply of a U-shaped tube of glass which is closed at one end, the closed limb being graduated and has two platinum wires fused near its extremity. This limb is to be filled with water, and then a given quantity of pure oxygen—20 cubic centimeters, for instance, is to be introduced from a delivery tube; 50 cubic centimeters of pure hydrogen is then similarly introduced, all measurements being made when the level of the

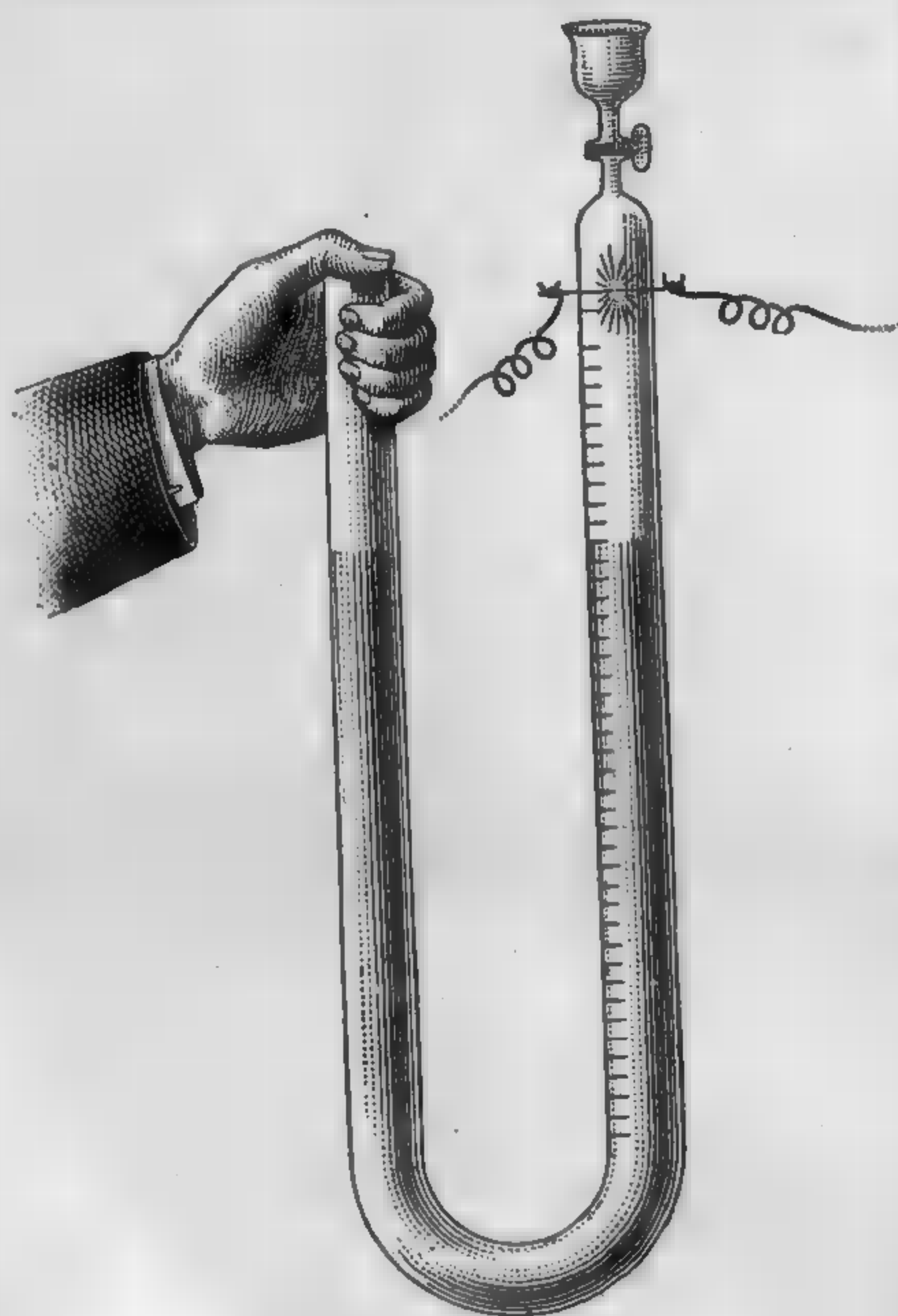
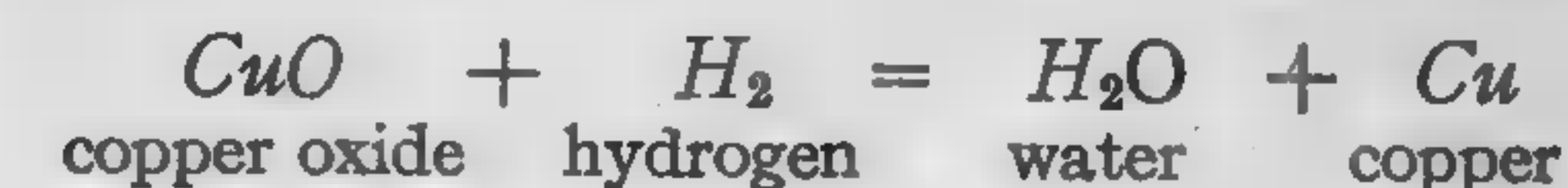


FIG. 17

liquid is the same in both limbs. The open end is closed firmly by the thumb, as represented in the drawing, a cushion of air being left between it and the liquid, and an electric spark is passed through the mixture of hydrogen and oxygen by means of the platinum wires. Upon restoring the level of the liquid by adding water, 10 cubic centimeters of gas will be left, which, on examination, will be found to be pure hydrogen. Hence, 20 volumes of oxygen has united with 40 volumes of hydrogen to form water, which is the ratio 1:2, required by theory and which is expressed by the formula H_2O .

38. Composition of Water by Weight.—The preceding experiments have shown the composition of water by volume, but it is necessary to become acquainted with the means employed for the determination of the exact composition by weight. The synthesis by weight cannot be effected with accuracy by weighing the gases themselves, on account of their large volume. It is therefore accomplished by passing

an indefinite quantity of hydrogen over a known weight of pure, hot oxide of copper, when hydrogen combines with the oxygen of the oxide to form water, according to the equation:



The loss of weight suffered by the oxide of copper gives the amount of oxygen; and, if this is deducted from the weight of the water, the weight of hydrogen will be ascertained.

The apparatus employed for this purpose is represented in Fig. 18.

EXPERIMENT.—The apparatus shown in Fig. 18 consists of a generating bottle *A*, in which hydrogen is evolved by the action of zinc and sulphuric acid. To this is attached a wash bottle *B*, partly filled with a solution of potassium hydrate, in order to retain any traces of sulphuric acid that may be carried over mechanically by the evolved hydrogen. To this wash bottle are attached, by means of leading tubes and stoppers, three U-shaped tubes *C*, *D*, and *E*. The tube *C* contains pumice moistened with a solution of mercuric chloride to absorb any hydrogen sulphide; the tube *D* contains fragments of fused potassium hydrate, which removes any carbon dioxide; and the tube *E* contains pumice moistened with strong sulphuric acid to dry the hydrogen. The object of the wash bottle and these three tubes is to remove all impurities from the evolved hydrogen, thus allowing only perfectly *pure* and *dry* hydrogen to pass into the bulb *F*. This bulb, or globe *F*, consists of a blown piece of combustion tubing which is attached to *E* by a piece of rubber tubing, and is in such a position that a Bunsen burner may be placed underneath it. The bulb *G*, also connected with *F* by a short piece of rubber tubing, is used for the collection of water, and is in turn connected with a drying tube *H*, filled with small pieces of calcium chloride.

Having this apparatus so far in readiness, about ½ ounce of perfectly dry copper oxide is placed in the bulb *F* and both are accurately weighed together. Then *G* and *H* are weighed separately and the apparatus reconnected, taking at the same time considerable care to make all joints perfectly air-tight.

By the addition of a small quantity of sulphuric acid to the generating bottle *A* through the funnel tube, in order to cause a slow evolution of hydrogen, the hydrogen passing through the entire outfit expels the air from it; as soon as pure hydrogen emerges from the jet *I*, the copper oxide in the bulb *F* is slowly heated by means of the Bunsen burner *J*. It will be soon noticed that water is produced and that it collects in receiver *G*, any traces of vapor being retained by the calcium chloride in *H*. After about 10 minutes, the burner *J* is removed and the bulb *F*

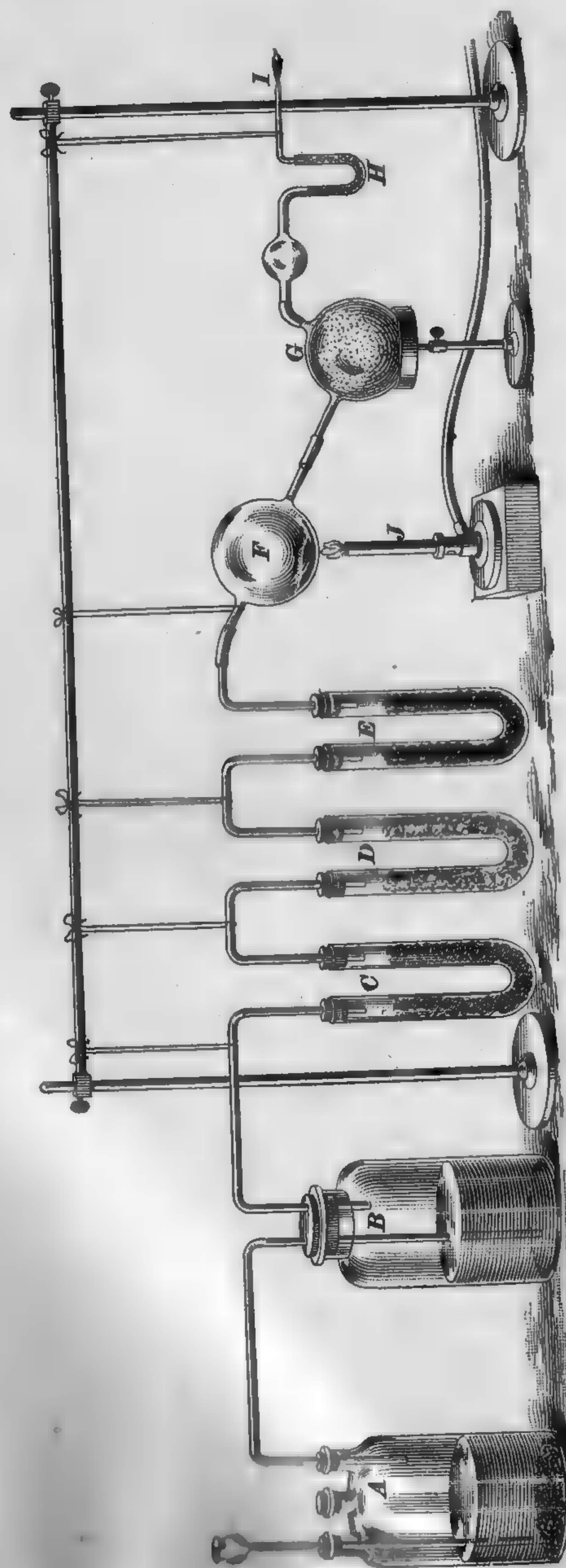


FIG. 18

allowed to cool. As soon as this bulb has thoroughly cooled, the apparatus is disconnected; the generating bottle *A* is first removed, and air drawn through the tubes by blowing into the glass tubing leading into the wash bottle *B*, so as to displace all hydrogen; then the copper-oxide globe *F* is disconnected and carefully weighed; the loss in weight represents the oxygen that has combined with hydrogen to form water. The bulb *G* and drying tube *H* are again weighed; their combined increase in weight is the water that has been produced.

Suppose, as the result of an actual experiment, that the copper oxide has lost 15.88 decigrams of oxygen, the receiver and drying tube will be found to have gained 17.88 decigrams in weight. We therefore would know that water contains 15.88 parts by weight of oxygen and 2 parts by weight of hydrogen in 17.88 parts of it, or 7.94 parts by weight of oxygen to 1 part by weight of hydrogen.

39. Oxyhydrogen Blowpipe.—By passing a jet of oxygen into a flame of hydrogen, a flame of the mixed gases is obtained, resulting in the production of the high temperature of 5,400° F. (2,982+° C.). By means of this arrangement a watch spring quickly burns while platinum can be readily melted, and silver distilled.

The principal part of the oxyhydrogen blowpipe, the nozzle, is shown in Fig. 19. The oxygen supply is connected with *O* and the hydrogen with *H*. The hydrogen is first ignited, after which the oxygen is turned on so that the flame burns quietly. In the nozzle illustrated there is no danger of an explosion due to a backward rush of the gas, as they mix only at the point at which the combustion takes place. When the oxygen is first turned on the size of the flame is

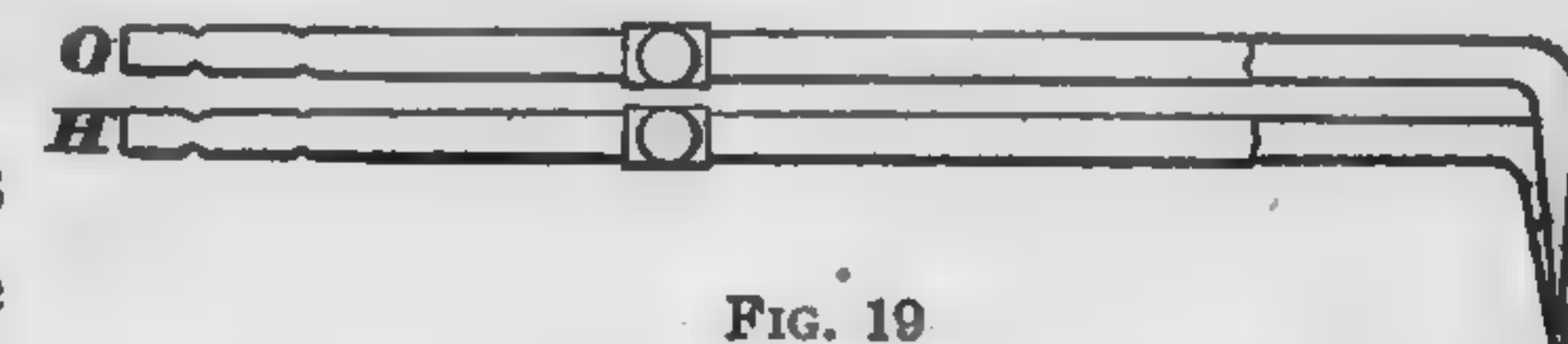


FIG. 19

greatly reduced, because the pure oxygen required to maintain the flame occupies only about one-fifth of the volume of the atmospheric air previously required. If a piece of some infusible and non-volatile substance such as lime is supported in the flame its temperature is raised to incandescence. The intense white light thus emitted is often used for illuminating purposes, under the name of the Drummond light.

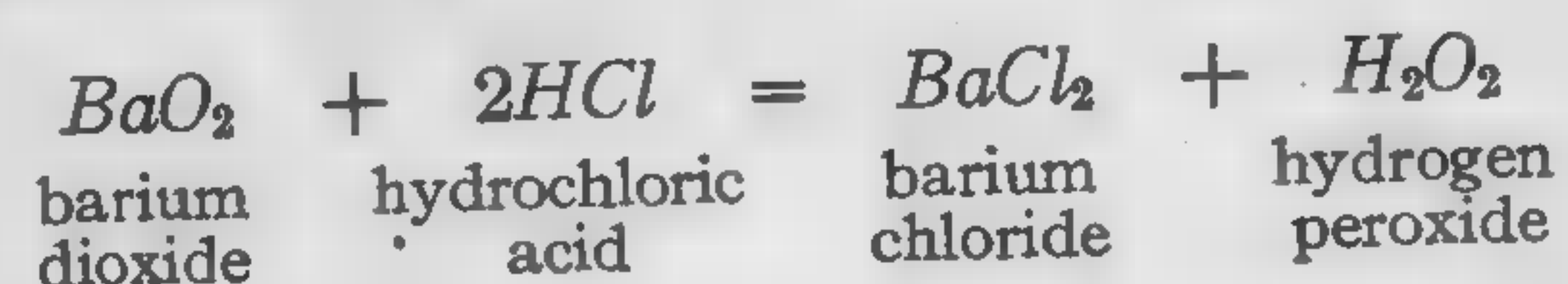
The high temperature of the oxyhydrogen flame is used in metallurgical processes such as the working of platinum, for metal cutting and for welding. For working platinum a block of carefully burnt lime is cut in two and each half is hollowed out to form the melting chamber. The upper half is perforated to allow the nozzle of the blowpipe to enter.

HYDROGEN PEROXIDE

Formula H_2O_2 . Molecular weight 34.016.

40. **History.**—This remarkable compound was discovered by Thenard in 1818, who called it *oxygenated water*.

41. **Preparation.**—Hydrogen peroxide, or dioxide, is prepared from barium dioxide by the action of hydrochloric or sulphuric acid. The reaction that occurs may be represented by the following equation:



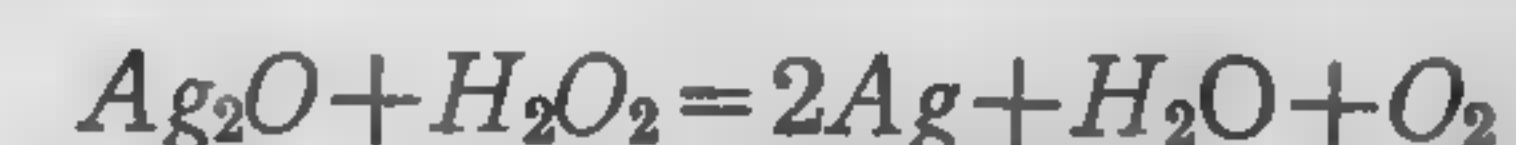
To prepare pure hydrogen peroxide, some barium dioxide, BaO_2 , is dissolved in as little dilute nitric acid as possible. To this solution one of barium hydrate, $Ba(OH)_2$, is added; the crystalline precipitate, $BaO_2 \cdot 8H_2O$, is washed by decantation, and gradually added to dilute sulphuric acid (1 part of acid to 6 parts of water, by weight), care being taken to leave the liquid very slightly acid; $BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4$. If the H_2SO_4 were added to the $BaO_2 \cdot 8H_2O$, instead as recommended, the H_2O_2 would be decomposed by the remaining BaO_2 as fast as it would be formed. The precipitate is allowed to settle, and the clear liquid evaporated in the exhausted receiver of an air pump, over a dish of sulphuric acid to absorb the water, which evaporates much more rapidly than the hydrogen peroxide.

42. **Properties.**—Pure hydrogen peroxide is a syrupy liquid having a strong acid reaction. It has a specific gravity of 1.458 at $0^\circ C$., boils at $69^\circ C$. under 26 mm. pressure, and at $85^\circ C$. under 65 mm. pressure. When viewed in bulk it has, like water, a bluish color, but is colorless in small quantities. It solidifies to anhydrous prisms, on cooling, which melt at $-2^\circ C$.

In the absence of direct sunlight and in a smooth container, hydrogen peroxide is fairly stable, while a container having a rough surface, continued shaking, or the presence of finely divided solid substances hastens decomposition. Aqueous solutions of hydrogen peroxide decompose slowly at low temperatures ($25^\circ C$.), losing oxygen, with the simultaneous formation of water, and at $100^\circ C$. the decomposition becomes very rapid, often causing explosions. Finely divided metals, such as platinum, gold, and silver, although having no direct attraction for oxygen, violently decompose hydrogen peroxide, without alteration of the metal.

From experiments it appears probable that this action of finely divided metals is an indirect one, the metal first acting on the air, rendering its oxygen active, the decomposition then taking place by the combination of the active oxygen with the extra oxygen atom of the hydrogen peroxide.

Hydrogen peroxide is at once decomposed, even in dilute aqueous solutions, by the oxides of gold, silver, and platinum, the oxides themselves being immediately reduced to metal. The following equation represents the reaction in the case of silver oxide:



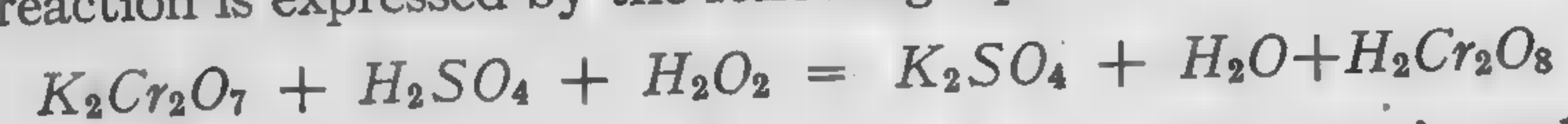
Here is seen the strange phenomenon of a powerful oxidizing agent acting as a reducing agent. This is explained by the fact that gold, silver, and platinum have only a feeble combining attraction for oxygen. Hence, when their oxides are brought into contact with hydrogen peroxide, which also contains an atom of oxygen feebly combined, a mutual reduction takes place, the two atoms of oxygen uniting to form an ordinary diatomic oxygen molecule.

Hydrogen peroxide acts as a strong bleaching agent and is largely used to bleach straw, silk, and wool. It is also used to bleach and clean engravings, ivory, and hair, and is used for medicinal purposes.

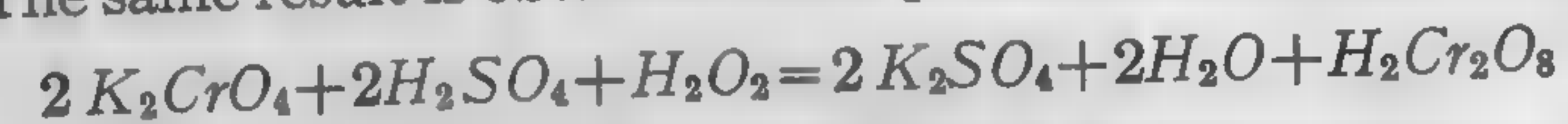
The exact constitution of hydrogen peroxide is not definitely known. It is generally believed to have the structural formula $H-O-O-H$, both atoms of oxygen being bivalent. Because of the ease with which one oxygen atom is evolved, however, one

atom of oxygen is supposed to be bivalent and one atom quadrivalent and the constitutional formula $\begin{smallmatrix} H \\ \diagup \\ O=O \\ \diagdown \\ H \end{smallmatrix}$ has been suggested. The formula $H-O\equiv O-H$, in which both oxygen atoms are quadrivalent, has also been proposed. This formula agrees better with certain physical constants of hydrogen peroxide than does the first, but from the fact that oxygen is usually bivalent the first formula is generally accepted as the correct one.

43. Tests.—The presence of hydrogen peroxide in a solution is detected by acidifying the solution with sulphuric acid, adding some ether and some potassium dichromate, and shaking the solution. If hydrogen peroxide is present a blue layer of perchromic acid in ether rises to the surface. The reaction is expressed by the following equation:

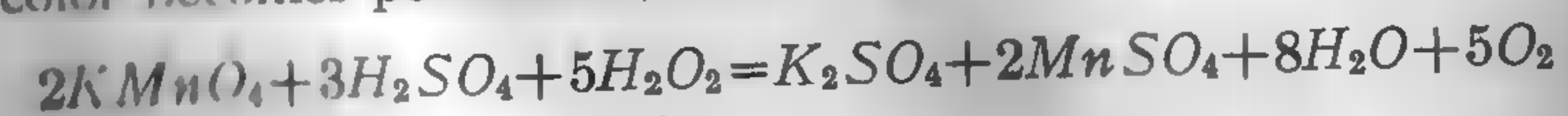


The same result is obtained when potassium chromate is used:



Titanic acid and vanadic acid turn red or brown when hydrogen peroxide is added to their solutions. A more delicate test is that of Schönbein's, namely, the action of the peroxide on a solution of potassium iodide and ferrous sulphate, liberating iodine and detection of the iodine by starch. While other oxidizing agents have the power of liberating iodine from potassium iodide, hydrogen peroxide is the only one that will liberate the iodine in the presence of ferrous sulphate.

The quantity of hydrogen peroxide in a solution can be determined by acidifying the solution with sulphuric acid and then adding a standard solution of potassium permanganate until the color becomes permanent, according to the following reaction:



44. Summary.—Water is a widely distributed liquid, which, however, owing to its great solvent power, is never found pure in nature. Heat changes its condition from solid to liquid, and from liquid to gas. Water is decomposed by

electricity into an explosive mixture of gases, each of which, however, may be separately collected; the gases recombine to again form water. By volume, water consists of 2 volumes of hydrogen and 1 of oxygen, which condense on union to form 2 volumes of steam. By weight, water contains 15.96 parts of oxygen to 2 parts of hydrogen.

Hydrogen peroxide, the second compound of oxygen and hydrogen, differs from water in that it contains an extra atom of oxygen in the molecule. This second atom is, however, held somewhat loosely; hence, this compound is readily decomposed into water and free oxygen. It acts as a reducing as well as an oxidizing agent.

INORGANIC CHEMISTRY

(PART 3)

CHEMICAL THEORY

MISCELLANEOUS MATTERS

DEFINITIONS AND DESCRIPTIONS

1. Oxidation and Combustion.—It has been seen that when a number of substances are heated and placed in oxygen they burn vigorously and form substances known as oxides. If pieces of iron or sodium having bright surfaces are exposed to the air for some time the surfaces become tarnished, and layers of the oxides of these metals will be formed on the surfaces. Thus, it is seen that whether the substance burns brilliantly, as in the case of charcoal, phosphorus, and the watch spring when placed in oxygen, or slowly becomes coated with a film of rust, as when iron or sodium is exposed to the air, the product in each case is an oxide. Hence, **oxidation** is the union of oxygen with other substances.

If the temperature of oxidizable substances is sufficiently high when they are brought in contact with oxygen, and the oxidation is sufficiently rapid so that the temperature is maintained and light is emitted during oxidation, the process is known as *combustion*. Hence, in its strictest sense, and the sense in which the term is most frequently used, **combustion** is the combination of substances with oxygen with evolution of light and heat. At times oxidation develops

considerable heat. Oily rags, piles of hay, and heaps of coal often take fire because of the heat developed by continued oxidation, giving rise to *spontaneous combustion*. Other chemical combinations, however, are accompanied by the evolution of heat and light; for instance, a jet of hydrogen lighted and placed in a vessel of chlorine will continue to burn, that is, the hydrogen unites with the chlorine with the evolution of heat and light, just as when it unites with oxygen; powdered antimony when thrown into a vessel of chlorine burns with nearly, if not quite, as great brilliancy as does iron, in the form of a watch spring, in oxygen. The term combustion is sometimes made to include these and similar cases, and, consequently, in its broadest sense combustion may be defined as any chemical act that is accompanied by the evolution of light and heat.

Oxidation is a broader term than combustion and includes all cases of combustion in its strictest sense, and also all cases of slow oxidation. If a fallen tree is ignited, it burns with the evolution of heat and light until all the combustible matter has been oxidized, and this is accomplished in a few minutes, or, at most, in a few hours. During the combustion the heat given off is so considerable that a person is obliged to remain at some distance from the burning tree. If the tree were allowed to lie undisturbed, the oxygen of the air would slowly attack it, and in time the combustible portion would be just as thoroughly oxidized as if the tree had been ignited and burned rapidly. Moreover, the amount of heat evolved in this case is exactly the same as if the tree had been ignited and burned rapidly, but as the heat is given off so slowly and during so long a time, it is scarcely perceptible. This slow combination with oxygen without evolution of light is called *slow oxidation*. In the case of the tree referred to, it would extend over many years. Cases of slow oxidation are seen daily. Implements of iron when exposed to damp air slowly unite with its oxygen, forming a coating of rust, which, of course, is oxide of iron. One of the most important instances of slow oxidation is that which takes place in our bodies. Large quantities of oxygen are taken into the lungs,

in the act of breathing, and here it comes in contact with, and oxidizes, impurities carried by the blood, changing them to substances that are easily thrown out of the system. Our food undergoes many changes, part of it being oxidized and thus keeping up the temperature of the body.

The term oxidation is further used in another sense. It has been stated that many of the elements show a different valence under different circumstances, and the act of increasing the valence of an element from a lower to a higher number is known as oxidation. Examples of this form of oxidation is the changing of a ferrous salt to a ferric, $FeCl_2$ to $FeCl_3$, stannous to stannic, $SnCl_2$ to $SnCl_4$, and sulphur dioxide to sulphur trioxide, SO_2 to SO_3 .

2. Kindling Temperature.—We have seen that at ordinary temperatures substances do not usually combine with oxygen, or only combine very slowly; but if the temperature is raised sufficiently, the union is rapid, and heat and light are given off. If small portions of phosphorus, sulphur, and carbon are subjected to a gradual increase in temperature, the phosphorus will soon ignite and burn vigorously; the sulphur will next ignite, and finally the carbon will burn. By repeating this experiment a number of times and carefully noting the temperature at which each substance ignites, it will be found that each one always ignites at the same temperature. By performing the same experiment with different substances, it has been found that every combustible substance has its *kindling temperature*, or *fixed ignition point*, and that below this point combustion will not take place, though slow oxidation will occur in many cases. If this were not the case, every combustible substance on the earth would immediately burn up by uniting with the oxygen of the air. Therefore, the **kindling temperature** of a substance is the temperature at which that substance will instantly unite with oxygen with the formation of heat and light.

If a piece of wood is ignited at one end, this portion is, of course, heated to the kindling temperature, and the heat generated by the combustion raises the surrounding portions

to this temperature, but at a distance of a few inches from the flame the wood is far below this temperature. Consequently, the flame creeps along slowly, the wood only igniting as it is raised to the kindling temperature by the approaching flame. If the wood were heated to its kindling temperature throughout its entire mass and then brought in contact with oxygen, its entire surface would burst into flame and it would be entirely consumed as fast as it could get the oxygen with which to unite.

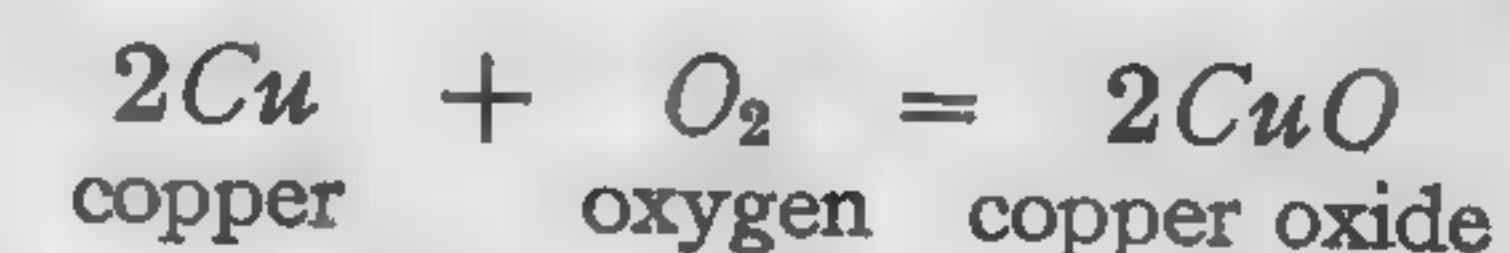
3. Explosion.—If every atom of carbon in the piece of wood just mentioned could get 2 atoms of oxygen when heated above its ignition point, the wood would be completely oxidized in an instant, with the formation of carbon dioxide. This gas would occupy many times the space taken up by the wood even at ordinary temperatures, but the heat of the combustion would cause it to expand and occupy much more space than it would at ordinary temperature. This sudden and great increase in volume causes a shock and manifestations of force that are accompanied by a detonation, and is known as an *explosion*. An *explosion* is extremely rapid combustion attended by a shock and more or less noise. The shock of an explosion is due to the sudden expansion of the gas formed when a substance is heated to a point considerably above its kindling temperature by rapid oxidation.

As a rule, an explosive body is composed of an intimate mixture of an inflammable substance and a supporter of combustion. For instance, if charcoal is ground together with potassium chlorate in sufficient quantity to furnish oxygen for the complete oxidation of the carbon, and the mixture is heated to its kindling temperature, the oxidation will be almost instantaneous, and an explosion will result.

Extremely rapid combustion, attended with more or less noise, is termed explosion; and the mixture that thus explodes is called an explosive body.

4. Oxidizing Agents.—An *oxidizing agent* may be defined as a substance that causes an element or compound to combine with oxygen or with other elements of similar

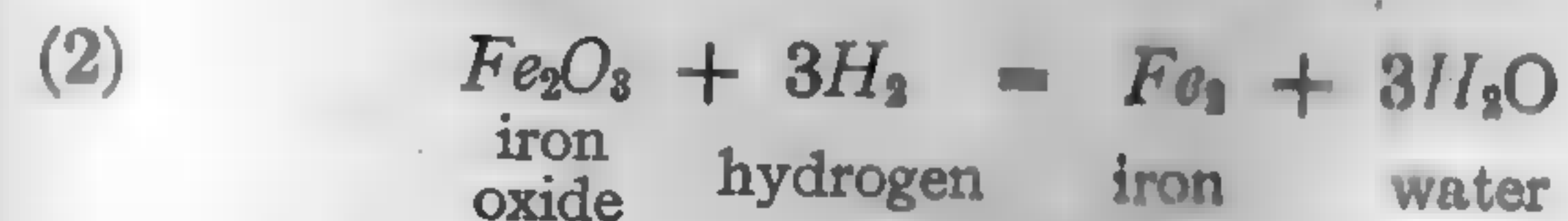
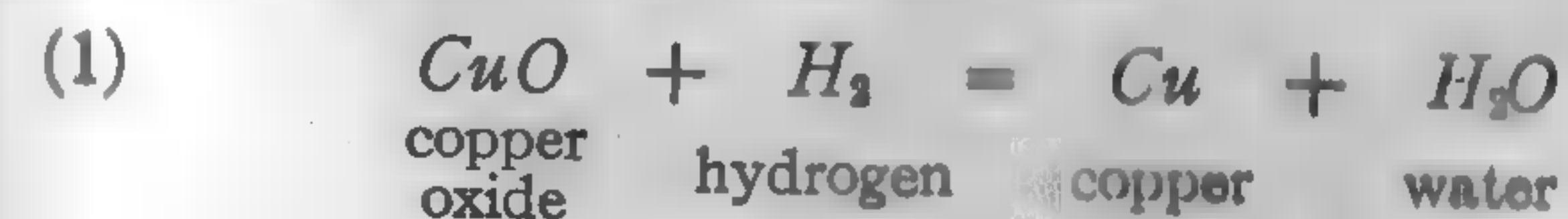
character or increases its valence. Oxygen and, to a greater degree, ozone are the most striking examples of oxidizing agents. If, for instance, metallic copper is heated in a current of oxygen, the following reaction takes place:



The following substances are some of the most frequently occurring oxidizing agents: Oxygen, ozone, chlorine, bromine, potassium chlorate, nitric acid, and hydrogen peroxide.

5. Reducing Agents.—The native compounds or ores, from which metals are derived, are in many cases oxides or sulphides of such metals. The process used to obtain these metals in a free or uncombined state is known as the reduction of the ore to its metallic state. From this we define a *reducing agent* as a substance that removes oxygen, or elements similar to it, from compounds, or decreases the valence of an element, changing it from a higher to a lower state of oxidation.

Owing to the activity with which hydrogen combines with oxygen, it is one of the most prominent and powerful reducing agents. Thus, if hydrogen is passed over red-hot copper oxide or iron oxide, the metal is obtained in the free state, according to the following equations:



It may here be mentioned, incidentally, that in this case hydrogen, a gas that may be produced by the reducing action of iron on steam, is passed over copper oxide, a product of the oxidizing influence of the oxygen of the air on copper.

The reaction of hydrogen on copper oxide is of great importance, as, in the analysis of many compounds containing hydrogen, the hydrogen is thus converted into water and weighed as such. In addition to these instances, in which a

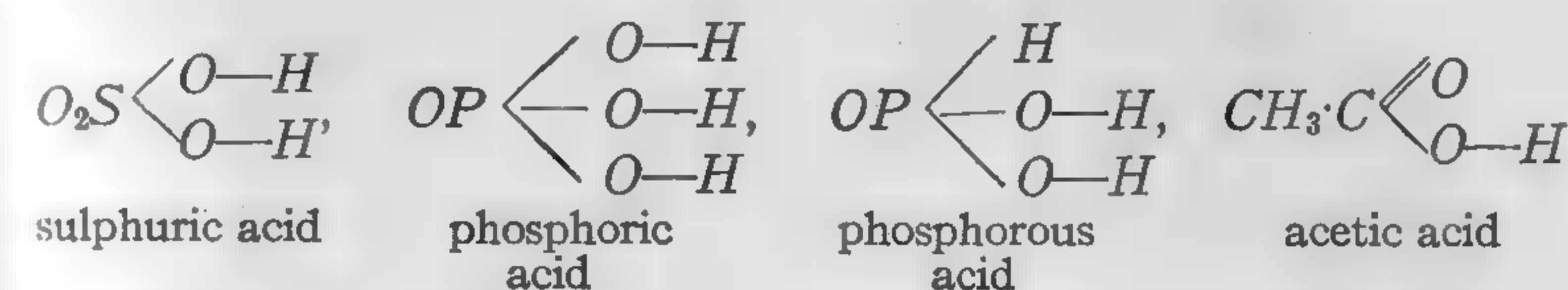
reducing agent is employed in order to obtain metals in their free state, there are other examples of reduction in which bodies are simply reduced to a lower state of oxidation. Further, the same reducing agents are capable of removing, in whole or in part, as the case may be, chlorine and other similar elements from compounds. Among the most active reducing agents, in addition to hydrogen, are: carbon, carbon monoxide, stannous chloride, and sulphurous acid.

6. Acids.—The name *acid* is a familiar one, because it is continually applied in every-day parlance to anything that is sour. A number of bodies possess this distinction in common; to the chemist the sourness of an acid is but an accidental property, as, according to his definition of these bodies, substances are included as acids that are not sour to the taste. An **acid** may be defined as a body containing hydrogen, which hydrogen may be replaced by a metal, or group of elements equivalent to a metal, to form a salt. It may also be defined as a compound that will unite with a base, forming a salt and water. As a class, the acids are sour; they are also active chemical agents. Most acids are characterized by the property of changing the color of a solution of litmus, a naturally blue body, to a red tint.

Oxygen is a constituent of most acids, the members of this group being distinguished as *oxyacids*. The oxides that by union with water form acids are termed *anhydrides*. They are in most cases non-metallic oxides, but sometimes consist of metals combined with a comparatively large number of atoms of oxygen. There are a few acids in which oxygen is absent; these are termed *hydracids*; hydrochloric acid, HCl , is an example of this class. According to the definition given, hydrogen is an essential constituent of all acids.

It has been found that in the oxyacids the hydrogen that is replaceable by metals is united to oxygen, forming the group $-O-H$. Some inorganic acids and many organic acids have only part of the hydrogen combined with oxygen, and it is only those hydrogen atoms that are thus combined with the

oxygen which are replaceable by a metal to form a salt with the acid. A glance at the graphic formulas of a few acids will probably show this clearly.



In all cases the $-O-H$ groups show the basicity of the acids, the number of replaceable hydrogen atoms. This, too, clearly shows the reason why phosphorous acid, although containing 3 atoms of hydrogen, is only capable of forming two classes of salts, instead of three as in the case of phosphoric acid. Again, this explains the reason for writing the formula of an acetate as $CH_3 \cdot COOM$ and why acetic acid has only one replaceable hydrogen atom instead of four, as might be naturally supposed from the formula.

As the non-metals are the usual acid-forming elements, an oxyacid may be considered as the **hydroxide**, or **hydrate**, of a non-metallic element or group.

7. Bases.—We have seen that the hydroxides of the non-metals are acids, and that the oxides of the non-metals bear a close relation to acids, in that they may become acids by the addition of water. On the other hand, the oxides and hydroxides or hydrates of the metals are known as *bases*. Hence, a **base** may be defined as a compound, usually an oxide or a hydrate, of a metal, or group of equivalent elements, capable of replacing the hydrogen of an acid. This property is so important that sometimes, instead of applying the name metals, this class of elements is called the base-forming elements. In chemical behavior the bases are the opposite of the acids, and their most distinguishing characteristic is their property of uniting with acids, forming salts and water. Among the most common bases are sodium hydroxide or hydrate, $NaOH$; potassium hydroxide or hydrate, KOH ; calcium hydroxide or hydrate, $Ca(OH)_2$, and calcium oxide (lime), CaO . The bases that dissolve in water are known as *alkalies*. The

leading members of this class are the hydroxides or hydrates of sodium and potassium. When ammonia gas is led into water, a compound NH_4OH , is in all probability formed. This acts in a manner similar in all respects to sodium and potassium hydrates, and is generally known as ammonium hydrate, the group $-N\equiv H_4$ acting like a metal. This is among the most common and useful of the alkalies.

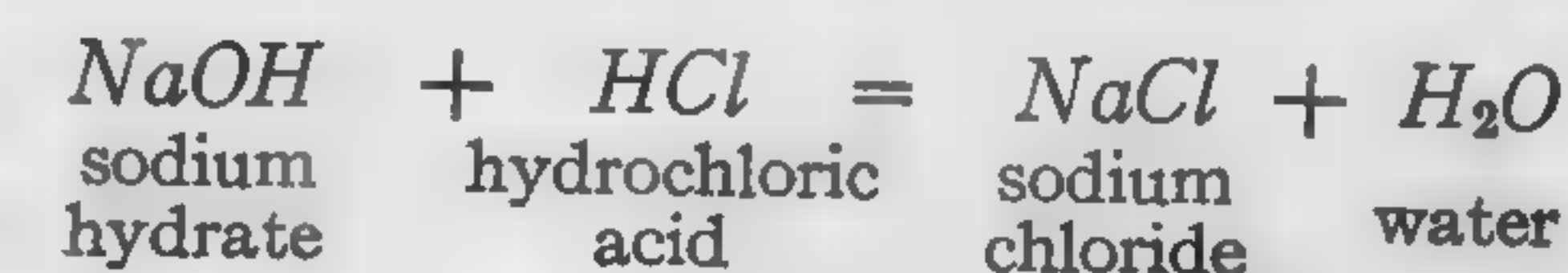
8. Neutralization.—A neutral solution of the vegetable dye litmus is blue in color. Solutions of acids have the power of changing this color to red, and solutions of bases in water have the power of restoring the blue color. For example, if two or three drops of hydrochloric acid are added to a neutral litmus solution, the color of the solution will be changed to a bright red. If, now, a few drops of a solution of sodium hydrate in water are added to the reddened litmus solution, the original blue color will be restored. By adding acid, the color of the solution may again be changed to red. When the red color is obtained, it is known as an acid reaction, and when the blue color is restored, it is known as an alkaline reaction. If the acid is very carefully added to the blue solution, the blue color will become less distinct at a certain point, and the solution, while still blue, will be found to have a slight reddish tint. At about this point the solution is neutral; that is, it is neither basic nor acid, the base and acid having neutralized, or destroyed, the properties of each other. This process of destroying basic and acid properties by allowing a base and acid to act on each other is known as **neutralization**.

The question now arises: Is a definite amount of acid required to neutralize a fixed amount of base? This can be shown definitely only by experiment. This may be tested by making up acid and alkaline solutions, say a solution of hydrochloric acid and one of sodium hydrate. Measure a certain quantity of the acid into a suitable vessel—a beaker, for example; add a little litmus solution and then slowly introduce the sodium hydrate solution from a graduated vessel until the neutral point is reached, which is indicated

when the last drop of alkali just gives the solution a blue color. Note carefully the exact amount of alkali solution used. By repeating this experiment several times and using different portions of the same solution, it will be found that exactly the same amount of alkali solution will be required each time to neutralize a given amount of acid, or that the same amount of acid will always be required to neutralize a given amount of alkali. Numerous experiments have shown that this holds good with all acids and alkalies.

9. Salts.—A **salt** is the product of the interaction of an acid and a base when the hydrogen of an acid is replaced by the metal of the base. It may also be defined as the solid substance that remains when the solution produced by the neutralization of an acid by a base is evaporated.

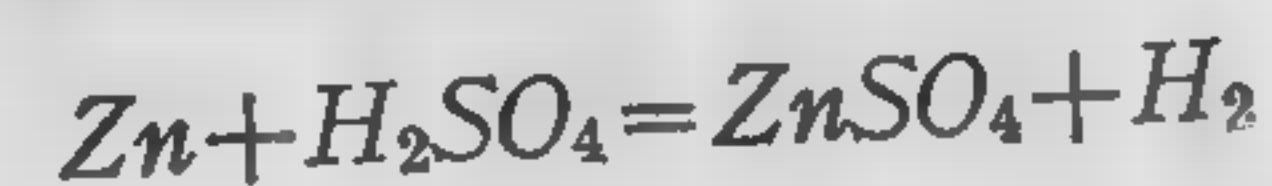
The salt which is most common is that known as sodium chloride, or common salt, which is formed according to the equation:



This substance has no effect on a litmus solution, nor does it in any way exhibit any acid or alkaline properties. In other words, the acid and alkaline properties of the two solutions that were mixed have been completely neutralized. This may be taken as a type of salts, which are substances produced by substituting the metal of a base for the replaceable hydrogen of an acid. Salts are of two kinds: those that contain oxygen, and those that do not. The salts whose names terminate in *ide* do not contain oxygen; those ending in *ate* do contain oxygen.

As a rule, salts are neutral in their action, but this is not universally the case, for when a strong acid acts on a weak base, the salt may have an acid reaction, as is the case with mercuric nitrate; and when a weak acid acts on a strong base, the salt formed may have an alkaline reaction. This is the case with sodium carbonate. It should be remembered that when a base and an acid act on each other, a salt

and water are formed. A salt may also be formed by the action of an acid on a metal, as shown by the equation:



It will be noticed that in this case water is not evolved.

10. Allotropy.—A number of the elements occur in different forms, having different properties. This is called **allotropy**, and is defined as the property some elements have of existing in more than one form. Ozone, an allotropic form of oxygen, is a good illustration. Other examples are the three varieties of carbon: diamond, graphite, and amorphous carbon. Phosphorus, arsenic, sulphur, and selenium all occur in several forms. The more uncommon form is called an **allotropic modification** of the other. It is probable that allotropy is due to a difference in internal molecular construction, and to a difference in the number of atoms in a molecule of the element.

11. Precipitation.—If we place some solution of mercuric chloride in a test tube and add to it, drop by drop, a solution of potassium iodide, a red powder is formed, which gradually settles down to the bottom of the tube. This powder is mercuric iodide, while potassium chloride remains in solution.

Whenever a substance separates from a solution through the addition of another, as the mercuric iodide has done in the example cited, the term *precipitate* is applied to the separated substance, and the substance that will produce a precipitate is known as a *precipitant*. Hence, **precipitation** is the process of causing the separation of a substance from a solution by the addition of another substance.

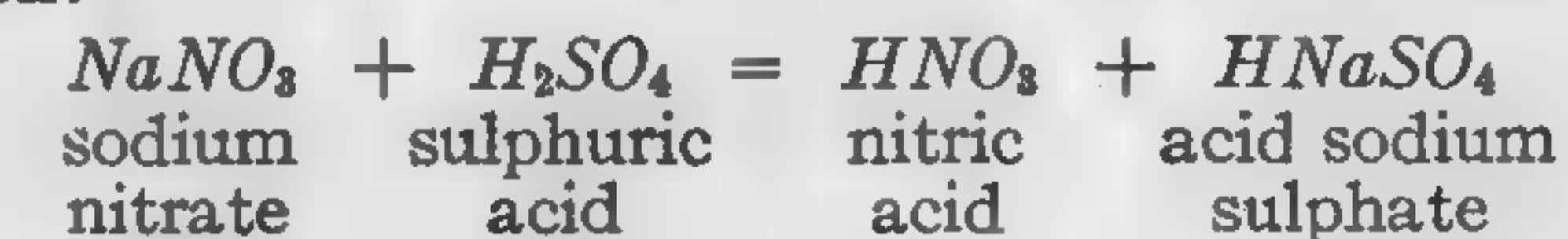
Those conditions of chemical change depending on solubility are stated in Berthollet's law, which may be expressed as follows:

When, on mixing two substances in solution, a new compound can be formed that is insoluble in the solvent employed, such compound will be formed and will appear as a precipitate.

12. Another law, also established by Berthollet, relates to the products of reactions that are volatile instead of being insoluble solids; it may be stated as follows:

When, on mixing different substances, a new substance that is volatile can be produced by the rearrangement of the atoms of the partaking substances, such new substance will be produced and will appear as a gas.

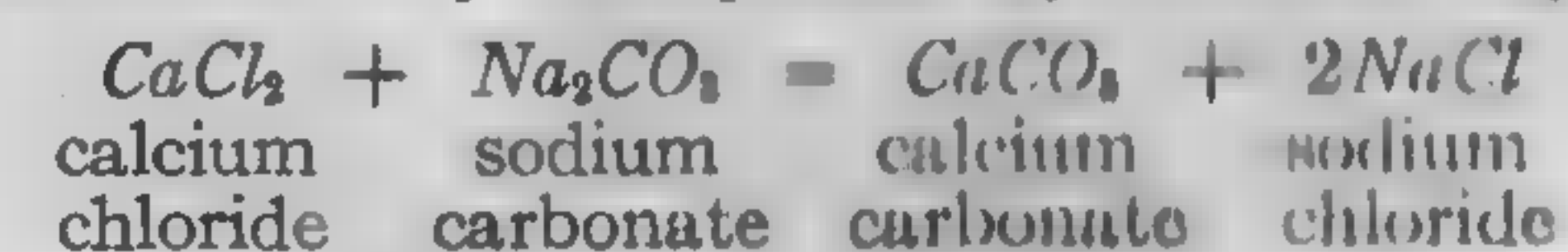
ILLUSTRATION 1.—If sodium nitrate, NaNO_3 , and sulphuric acid, H_2SO_4 , are mixed together, through a rearrangement of the atoms of these two substances, acid sodium sulphate and nitric acid are produced, according to the equation:



Nitric acid, being volatile, escapes as a gas when heat is applied.

By means of Table I, which shows the solubility of various compounds, the resulting chemical change of these compounds, covered by the first-mentioned law of Berthollet, may be predicted, and as the student progresses in his study and experimenting he will soon acquire sufficient knowledge to predict also the changes covered by the second-mentioned law of Berthollet, which requires some familiarity with the volatility of the various compounds.

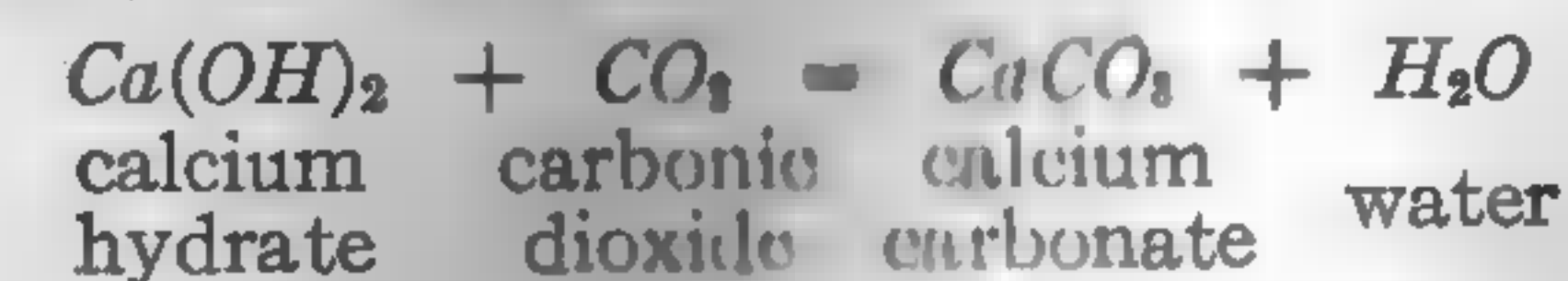
ILLUSTRATION 2.—The reactions obtained by mixing calcium chloride and sodium carbonate may be expressed by the following equation:



Will there be a precipitate?

By consulting Table I, it will be found that calcium carbonate is insoluble, and it can be predicted that under the given conditions calcium carbonate will be obtained in the solid form as a precipitate.

The reactions obtained by mixing calcium hydrate and carbon dioxide may be expressed by the equation:



Will there be a precipitate?

By consulting Table I it will be found that calcium carbonate is insoluble in water, and therefore it can be predicted that under the given conditions calcium carbonate will be obtained as a precipitate.

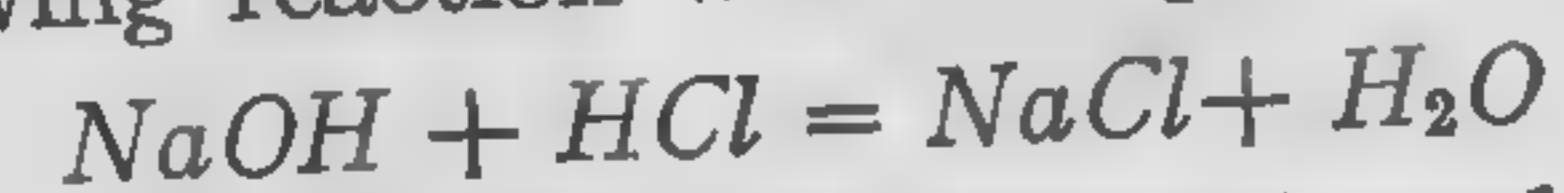
TABLE I
SOLUBILITIES OF CHEMICAL COMPOUNDS

	Platinic	Auric	Mercuric	Mercurous	Lead	Arsenic	Antimonic	Stannic	Stannous	Silver	Bismuth	Cupric	Cadmium	Ferric
Hydrate.....	A	A	A	A	A	DW	A-I	A-I	A	A	A	A	A	A
Nitrate.....	W	W	W	W	W			W	A	W	W	W	W	W
Carbonate.....	A		W	A	A			W	W	DW	W	W	W	W
Acetate.....		W	W	W	W		A	W	W	A	W	W	W	W
Oxalate.....	W	W	W	W	W		A	W	W	A	W	W	W	W
Cyanide.....	DA	W	W	W	DW	W	W	W	W	I	W	W	W	W
Chloride.....	W	W	W	W	DW	W	W	W	DW	I	W	W	W	W
Bromide.....	W	W	W	W	DW	DW	W	DW	W	I	W	DW	W	W
Iodide.....	A	W	DA	A	A	W	W	DW	W	W	W	W	W	W
Fluoride.....	W	W	W	W	A	A	W	DW	W	W	W	W	W	W
Sulphide.....	W	W	W	W	A	A	W	DW	W	W	W	W	W	W
Sulphite.....	W	W	W	W	A	A	W	DW	W	W	W	W	W	W
Sulphate.....	W	W	W	W	A	W	W	DW	W	DW	W	W	W	W
Phosphate.....		A	DW	A	DW		W	A	DW	DW	DW	DW	DW	DW
Borate.....														
Silicate.....			A	A	A		W	A	A	A		A		A
Arsenite.....			A	A	A		A	A	A	A		A		A
Chromate.....	A													

	Aluminum	Chromium	Cobalt	Nickel	Manganese	Zinc	Barium	Strontium	Calcium	Magnesium	Sodium	Ammonium	Potassium	Hydrogen
Hydrate.....	A	A-I	A	A	A	A	DW	DW	DW	A	W	W	W	W
Nitrate.....	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Carbonate.....	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Acetate.....	A	W	W	W	W	W	W	W	W	W	W	W	W	W
Oxalate.....		W	W	W	W	W	W	W	W	W	W	W	W	W
Cyanide.....	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Chloride.....	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Bromide.....	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Iodide.....	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Fluoride.....	A-I	W	DW	DW	W	DW	W	A-I	W	W	W	W	W	W
Sulphide.....	A	W	A	A	A	A	W	W	W	W	W	W	W	W
Sulphite.....	A	W	W	W	W	DW	A	W	W	W	W	W	W	W
Sulphate.....	W	W	W	W	W	W	I	A	DW	W	W	W	W	W
Phosphate.....	A	W	W	W	W	W	A	A	A	A	W	W	W	W
Borate.....	DW	DW	DW	DW	DW	DW	DW	DW	DW	DW	DW	DW	DW	DW
Silicate.....	A-I						A	A	A-I	A-I	W	W	W	W-I
Arsenite.....			A	A	A	A	DW	DW	A		W	W	W	W
Chromate.....		A	DW	W	W	W	A	DW	DW	W	W	W	W	W

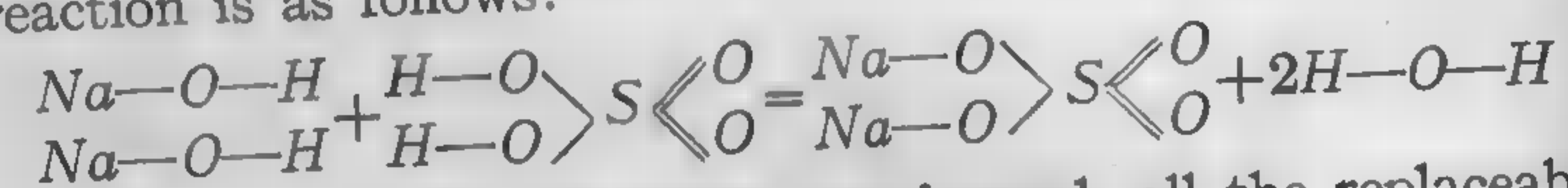
W means soluble in water; A, soluble in acids; I, insoluble in water and hydrochloric or nitric acid; DW, difficultly soluble in water; DA, difficultly soluble in acids.

13. Basicity of Acids.—It is found, when working with acids and bases, that certain acids have the power to form only one salt with bases like sodium hydrate. Thus, if a quantity of sodium hydrate is neutralized by hydrochloric acid, the following reaction will take place:

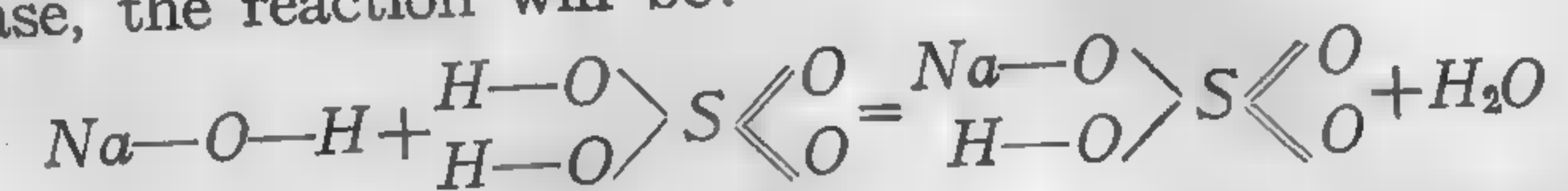


Sodium chloride and water are formed, and no other result can be obtained by any change in the proportion of acid and base in the mixture. If half the acid required to neutralize the base were added, half of the base would be changed to sodium chloride, and the remainder would continue in its original condition and thus be mixed with the salt. If twice the required amount of acid were added, the half necessary to neutralize the base would be used up, and the other half would remain in the solution in its original condition. This can be evaporated off with the water, leaving the pure salt.

If sodium hydrate is neutralized by sulphuric acid, the reaction is as follows:



Sodium sulphate and water are formed, all the replaceable hydrogen has been removed, and the salt is neutral. If, now, the same amount of acid is mixed with half the amount of base, the reaction will be:



In this case only half of the replaceable hydrogen is removed, and the resulting compound has the properties both of an acid and a salt. It is an acid salt and is usually called acid sodium sulphate, but the names sodium bisulphate and hydro-sodium sulphate are also applied to it. Acids like sulphuric are capable of forming salts containing two metals, each metal replacing an atom of hydrogen.

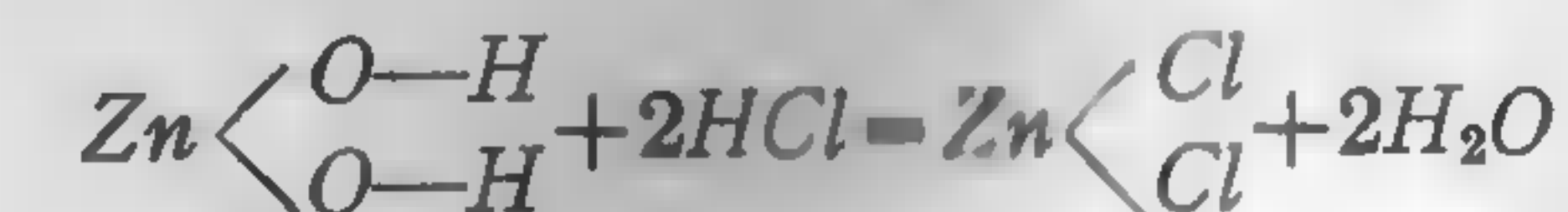
Acids like hydrochloric have the power to form but one salt with bases like sodium hydrate. When the 1 atom of hydrogen in each molecule is replaced by a metal, no further action is possible, and the result is a neutral or *normal* salt.

Such acids are known as monobasic. Sulphuric acid may have half its hydrogen removed, forming an acid salt, or all of its hydrogen replaced, forming a normal salt. Such acids are known as dibasic.

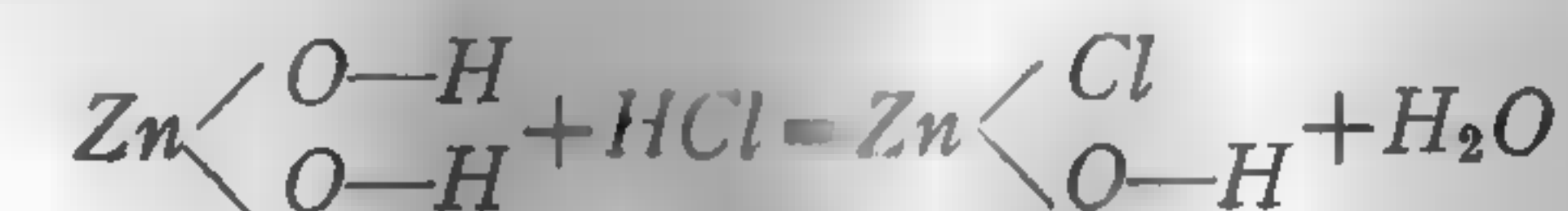
The *basicity of an acid is its power of uniting with a base to form a salt, and depends on the amount of replaceable hydrogen it contains*. Acids like hydrochloric, that contain 1 atom of replaceable hydrogen, are called *monobasic*; those like sulphuric, that contain 2 atoms of replaceable hydrogen, are called *dibasic*; those like phosphoric, that contain 3 atoms, are called *tribasic*; those like pyrophosphoric, that contain 4 atoms, are called *tetrabasic*; and those like periodic, that contain 5 atoms of replaceable hydrogen, are called *pentabasic*. The greater number of atoms of replaceable hydrogen an acid has, the greater the number of salts it can form.

14. Acidity of Bases.—Just as acids are classified as monobasic, dibasic, tribasic, tetrabasic, etc., so bases are classified as monacid, diacid, triacid, etc., according to the amount of acid hydrogen they are capable of replacing.

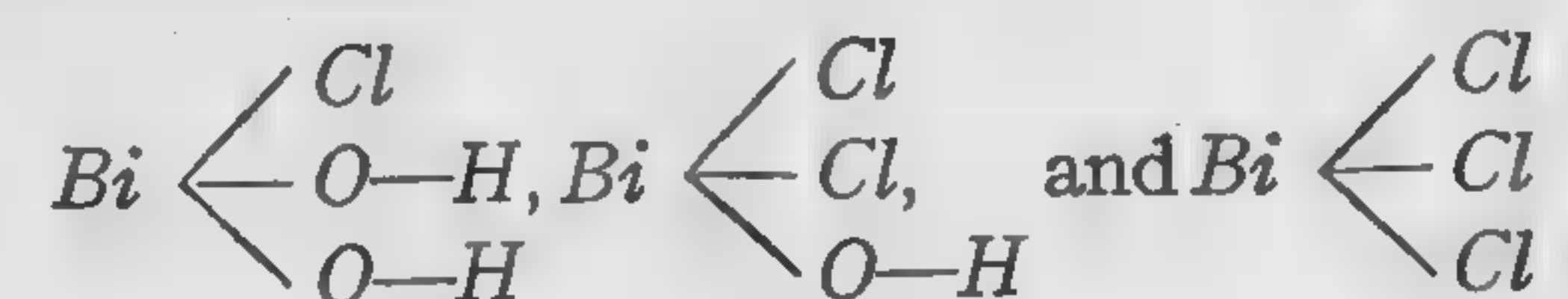
The *acidity of a base is its capability of replacing the hydrogen atoms of an acid*. Bases like sodium and potassium hydrates, that can only replace 1 atom of acid hydrogen, are called *monacid bases*. When a monacid base is acted on by a monobasic acid, a normal salt is formed, and, as a rule, no other reaction is possible. Bases like calcium oxide and zinc hydrate, that are capable of replacing 2 atoms of hydrogen, are known as *diacid bases*. When a monobasic acid acts on one of these, two salts may be formed. For instance, if a quantity of zinc hydrate is neutralized with hydrochloric acid the reaction will be:



The salt formed (zinc chloride) will be normal and have neutral properties. If the same amount of zinc hydrate is treated with half the quantity of hydrochloric acid, the reaction will be:



In this case only half the hydroxyl of the base is removed, and the resulting compound retains basic properties. It also has the properties of a salt. In fact, it is a basic salt known as basic zinc chloride. Triacid bases like ferric oxide, Fe_2O_3 , and bismuth hydrate, $Bi(OH)_3$, are capable of forming three classes of salts. For instance, if bismuth hydrate is treated with varying quantities of hydrochloric acid, the following salts may be formed:

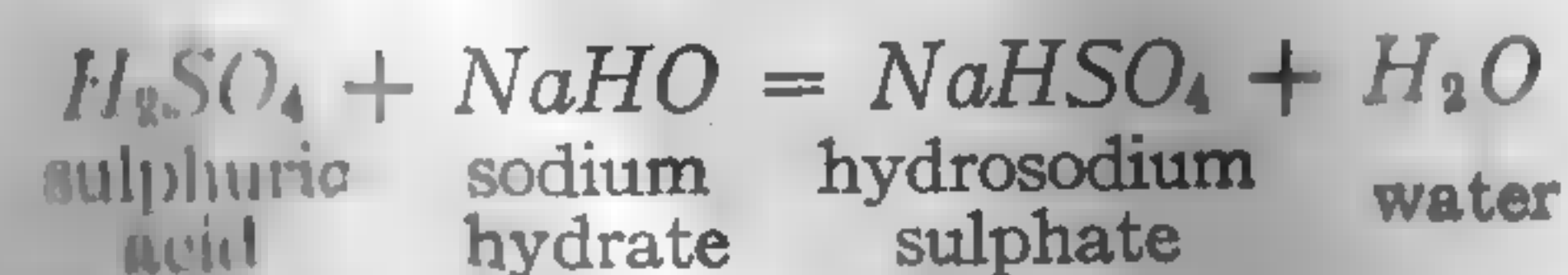


The latter is normal bismuth chloride, and the other two are basic chlorides. From the preceding it will be evident that the greater the number of acid hydrogen atoms a base is capable of replacing, the greater the number and variety of salts it can form.

15. Normal, Acid, and Basic Salts.—From the preceding articles it is seen that there are three kinds of salts, known as *normal*, *acid*, and *basic* salts. The term acid and basic as used in connection with salts does not refer to their acid or alkaline properties toward litmus or other indicators. It refers simply to the quantity of hydrogen of the acid, or excess of metal of the base remaining unneutralized. For example, sodium bicarbonate, $NaHCO_3$, although an acid salt, is slightly alkaline to litmus paper.

A **normal salt** may be defined as a salt produced by the replacement of the hydrogen of the acid by its valence equivalent of a metal, or by a group of elements that acts as a metal, in a base.

In the case of those acids containing more than 1 replaceable atom of hydrogen, if a portion only of such hydrogen is replaced, the result is a salt that still possesses an acid character. An **acid salt** may, then, be defined as a salt produced by the partial replacement of the hydrogen atoms of a polybasic acid by the metal of a base; as, for instance:



Certain oxyacids exist that possess the power of combining with more of the base than is necessary to produce a normal salt, thereby forming what are termed *basic salts*. A **basic salt** may, then, be defined as a salt produced by the combination of an acid with a higher proportion of a base than is necessary for the formation of a normal salt. Yellow basic mercuric sulphate, known as turpeth mineral, is an example of a basic salt, the additional quantity of base being distinguished here by being placed after the comma in the formula $HgSO_4, (HgO)_2$. Its formula is generally written thus: $Hg_3(SO_4)_2$.

16. Oxygen and Acid Properties.—By far the greater number of acids contain oxygen, and it was because this element was believed to be the essential constituent of acids that it received the name **oxygen**, which means the acid former. It is now known that hydrochloric and several similar acids do not contain oxygen, and consequently that it is not essential to acids. It apparently has acid properties, however, for when introduced into certain basic groups in sufficient quantity it changes them to acids. On the other hand, there are compounds analogous in composition to the oxyacids, but which do not contain any oxygen, that have acid properties. For instance, there is a compound analogous to arsenic acid, having the formula H_3AsS_4 , known as *sulphar-arsenic acid*. If potassium hydrosulphide is treated with this compound, the following reaction takes place:



The analogy between this acid and the corresponding acid containing oxygen may be seen by changing each S in the above equation to O. By so doing, the equation will be obtained that shows the reaction that takes place when arsenic acid acts on potassium hydrate. The fact that other elements form compounds having the same form and much the same properties as the oxyacids, makes it appear that acid forming is a general property possessed by several of the non-metallic elements.

NOMENCLATURE

17. Nomenclature of Acids.—The names of the acids are derived from those of their principal constituents, changing them into adjectives, with the name of the principal acid of the series ending in *ic*. As an illustration of this, sulphuric acid may be mentioned. If the principal element forms but two acids, the one containing the greater proportion of oxygen has the suffix *ic*, and the one containing the lesser amount ends in *ous*. This also holds good in case an element forms a series of acids. In the case of the acids of sulphur, the principal one, H_2SO_4 , is called sulphuric acid. A second acid, H_2SO_3 , containing less oxygen, is called sulphurous acid. But there is another acid of sulphur, H_2SO_2 , containing still less oxygen than sulphurous acid. This is called hyposulphurous acid. Thus it is seen that an acid containing less oxygen than that having the suffix *ous* is designated by the prefix *hypo* (from the Greek word for under) and the suffix *ous*. In some cases there are acids having a greater proportion of oxygen than the acid ending in *ic*. These are designated by the prefix *per* and the suffix *ic*. For example, there is an acid of chlorine having more oxygen than chloric acid, and it is consequently called perchloric acid. This system will cover the great majority of cases, but there are some cases in which all the acids would not be included in this system. These are of a more or less special nature, however, and names are given according to circumstances.

What has been said refers to oxygen acids, but there are a few acids that do not contain oxygen, but consist of hydrogen united directly with the principal element. These are known as hydracids, and are designated by means of the prefix *hydro* and the suffix *ic*. Examples of this class of acids are hydrochloric acid, HCl ; hydrobromic acid, HBr , and hydrosulphuric acid, H_2S .

This system of nomenclature of the acids is well illustrated by the series of chlorine acids in Table II.

Oxyacids are sometimes divided into *ortho*- and *meta*-acids, but this distinction is not important and these terms are

often used in a rather loose way. In its strictest sense, an *ortho*-acid is one containing as many hydroxyl groups as the maximum valence of the principal element. Thus, phosphorus, having a maximum valence of 5 (as is shown by the formation of PCl_5), might be expected to form an acid having the formula $P(OH)_5$, and this would be called *ortho-phosphoric* acid. As a matter of fact, this acid is not known, and only a very few acids formed in this way do exist; hence, the term is often used in a broader sense and is applied to the normal tribasic acids. Thus, $PO(OH)_3$ is frequently called *ortho-phosphoric* acid.

A *meta*-acid is one formed by extracting water from an *ortho*-acid. Hence, if we use the term *ortho* in its strictest sense in the case just mentioned,

and call $P(OH)_5$ *ortho-phosphoric* acid, the acid usually called *ortho-phosphoric*, $PO(OH)_3$, which would be formed by removing one molecule of water from $P(OH)_5$, would be a *meta*-acid; and by removing another molecule of water we would have another *meta*-acid, $PO_2(OH)$, which is usually known as *meta-phosphoric* acid. Thus,

we would have two *meta*-acids of phosphorus. To avoid confusion, when the term *ortho* is used in its strictest sense, the term *anhydro-acids* is sometimes applied to those obtained by the removal of water from the *ortho*-acids, and the term *meta* is reserved for a particular acid. This distinction is only important in studying the theoretical formation of acids, but the terms *ortho* and *meta* are important in organic chemistry where they are applied in a different manner.

TABLE II
ACIDS OF CHLORINE

Acid	Formula
Hydrochloric..	HCl
Hypochlorous.	$HClO$
Chlorous.....	$HClO_2$
Chloric.....	$HClO_3$
Perchloric....	$HClO_4$

18. Nomenclature of Bases.—As previously stated, the bases are oxides or hydrates of the metals; that is, they are combinations of metals with oxygen or oxygen and hydrogen in the form of the hydroxyl group, $-O-H$. In order

to distinguish between the different oxides and hydrates, the names of the metals are put before the name oxide, hydrate, or hydroxide. Thus, NaOH is known as sodium hydrate or sodium hydroxide; Ca(OH)_2 as calcium hydrate or calcium hydroxide; K_2O as potassium oxide, and BaO as barium oxide. Some metals form two sets of bases having different degrees of oxidation. These are named by changing the name of the metal to the adjective ending in *ic* in the case of the one having the most oxygen, and in *ous* in the case of the one having the least oxygen, thus following the general rule. For example, FeO is ferrous oxide, and Fe_2O_3 is ferric oxide; Fe(OH)_2 is ferrous hydrate or ferrous hydroxide, and Fe(OH)_3 is ferric hydrate or ferric hydroxide.

It will be noticed that the terms hydrate and hydroxide as used above have the same meaning. The terms are thus used in most books on chemistry, and this usage will, therefore, be adopted in these Sections. Strictly speaking, however, the term hydroxide is the best, as the word hydrate indicates that the substance is derived from water, or contains water as such, whereas the term hydroxide merely indicates that the substance contains the hydroxyl group ($-\text{O}-\text{H}$).

19. Nomenclature of Salts.—Theoretically, every metal can form a salt with every acid, and consequently there are many salts of each of the acids. The salts of each of the acids receive a general name, and this is qualified by placing the name of the metal contained in the salt before the general name. Thus, the salts of sulphuric acid are called sulphates, and the salt produced by the action of sulphuric acid on potassium hydroxide is called potassium sulphate.* If the name of the acid ends in *ic*, the name of its salts will end in *ate*. Thus, sulphuric acid yields sulphates; nitric acid, nitrates; chloric acid, chlorates, etc. If the name of the acid ends in *ous*, the name of the salts will end in *ite*. Thus, sulphurous acid yields sulphites; nitrous acid, nitrites, etc. Prefixes added to the name of the acid also appear in the name of the salts, as, for example, hyposulphurous acid yields hyposulphites, perchloric acid yields perchlorates, etc.

Some metals form two salts with the same acid. In such cases the salt in which the metal acts with the lower valence is designated by the suffix *ous*, and that in which it acts with the greater valence has the suffix *ic*. Thus, iron forms two salts with sulphuric acid, FeSO_4 , known as ferrous sulphate, and $\text{Fe}_2(\text{SO}_4)_3$, known as ferric sulphate. Tin forms two salts with hydrochloric acid, SnCl_2 , known as stannous chloride, and SnCl_4 , known as stannic chloride.

If the salts of hydrochloric acid were named according to the principles just explained, they would be called hydrochlorates, but as the salts of hydrochloric acid have the same composition as the compounds formed by the action of chlorine on the metals, the name chloride, which is applied in the case of the direct union of the two elements, applies also in the case of the action of the base and acid on each other. Consequently, the name hydrochlorate is unnecessary. The same is true of the other hydracids, their salts being named according to the principles adopted for naming binary compounds.

20. Nomenclature of Binary Compounds.—Binary compounds, as the name indicates, are those containing but two elements or groups acting as elements. The names of binary molecules are derived from their constituent atoms.

The most frequently occurring binaries are those composed of a metal and a non-metal; the name of the metal is written first, and then that of the non-metal, one or more syllables being removed from the latter, and the termination *ide* added.

ILLUSTRATION.—

Copper and oxygen yield copper oxide.
Magnesium and oxygen yield magnesium oxide.
Silver and sulphur yield silver sulphide.
Zinc and phosphorus yield zinc phosphide.
Calcium and iodine yield calcium iodide.
Aluminum and bromine yield aluminum bromide.
Sodium and chlorine yield sodium chloride.
Potassium and nitrogen yield potassium nitride.
Barium and fluorine yield barium fluoride.
Cadmium and selenium yield cadmium selenide.

The termination *ide* is always characteristic of a binary compound.

Whenever the metal atom enters into combination with more than one valence, this fact is indicated in the compound by changing the termination of the name of this atom into *ic* or *ous*. Should the metal act with only two valences, then in the higher one its name takes the termination *ic*, and in the lower one the termination *ous*.

ILLUSTRATION.—

Bivalent mercury and oxygen yield mercuric oxide.
Univalent mercury and oxygen yield mercurous oxide.
Quadrivalent tin and chlorine yield stannic chloride.
Bivalent tin and chlorine yield stannous chloride.

If the metallic constituent acts with more than two valences, the termination *ic*—being given on the discovery of the compound—is generally arbitrarily assigned, and a further discrimination becomes again necessary; this distinction is marked by the use of a prefix. A compound in which the valence of the first, or metallic, constituent is *less* than in the *ous*, takes the prefix *hypo*, which means *under*. When the valence is above *ic*, the prefix *per* is used. The termination of the second constituent, however, always remains *ide*.

ILLUSTRATION.—

Pentavalent chlorine and oxygen form chloric oxide.
Trivalent chlorine and oxygen form chlorous oxide.
Univalent chlorine and oxygen form hypochlorous oxide.
Septivalent chlorine and oxygen form perchloric oxide.
Sexivalent sulphur and oxygen form sulphuric oxide.
Quadrivalent sulphur and oxygen form sulphurous oxide.
Bivalent sulphur and oxygen form hyposulphurous oxide.
Pentavalent nitrogen and oxygen form nitric oxide.
Trivalent nitrogen and oxygen form nitrous oxide.
Univalent nitrogen and oxygen form hyponitrous oxide.

Instead of using the suffixes *ic* and *ous*, numerals are sometimes prefixed to the adjective, as, for instance, in the case of the oxides of carbon. The compound CO is known as carbon monoxide, and CO_2 is known as carbon dioxide; P_2O_5 is called phosphorus pentoxide, etc.

There are a few cases in which the names of compounds containing more than two elements end in *ide*; but there are only a few such cases, for example, the cyanides, compounds containing the group $C\equiv N$, and hydroxides, which contain the group $O-H$. These compounds are similar to the binaries in many respects. Some chemists avoid the ending *ide* in case of the hydroxides by calling these compounds hydrates. This would indicate that these compounds are salts of water, which in this case would be considered as hydric acid. Water, however, does not possess the general properties of an acid, nor do the hydroxides have the general properties of salts. It is better to regard water as a neutral substance, and the hydroxides as bases.

VOLUME RELATIONS OF MOLECULES

21. Combination by Volume.—Gay-Lussac, who investigated the proportions in which gaseous volumes enter into combination, established the following laws:

1. *The ratio in which gases combine by volume is always a simple one.*
2. *The volume of the resulting gaseous product bears a simple ratio to the volume of its constituents.*

The laws of combination by volume, which at the time of Gay-Lussac's investigation (between 1805 and 1808) were simply experimental, have recently been investigated by Clausius, who has shown that they are really nothing but a very simple deduction from the law of Avogadro.

According to Avogadro's law, equal volumes of all gaseous bodies contain the same number of molecules. If, therefore, the number of molecules is in some way decreased, the volume must necessarily be decreased also. If we assume that in a given volume of any gas each molecule is diatomic, and that by some means the molecule can be made tetratomic—the number of atoms remaining the same—the number of molecules will be reduced one-half, since each molecule contains twice the number of atoms; and this reduction of mole-

cules is naturally accompanied by a corresponding decrease of the volume; that is, the volume of the gas will also be reduced one-half.

Or, if we assume that the diatomic molecule could be made triatomic, the number of molecules, and consequently the volume, would be reduced one-third.

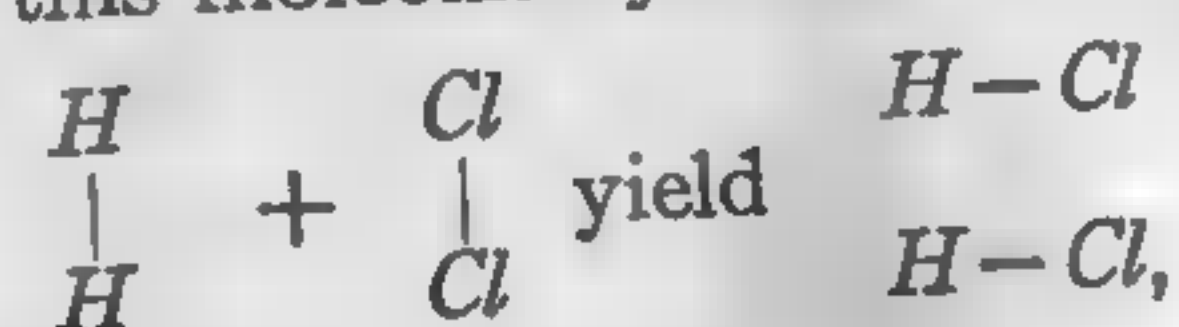
To apply this argument to the facts of volume combination, we will consider separately the combination of hydrogen with monads, dyads, triads, and tetrads, assuming all their molecules to be diatomic.

1. *Combination of a Monad With Hydrogen.*—Each atom of a monad combines with an atom of hydrogen; before they combine, their molecules are each diatomic, and each molecule of the compound is also diatomic; if there was 1 volume of each before the combination, the number of compound molecules after the combination takes place is exactly equal to the sum of the molecules of the monad and hydrogen before they combined, and the result is 2 volumes of the compound.

Monads, then, combine with one another, volume to volume, yielding 2 volumes of the product.

ILLUSTRATION 1.—The monad atom chlorine, *Cl*, and the monad atom hydrogen, *H*, combine to form hydrochloric acid, *HCl*. Their molecules being diatomic, they unite, molecule to molecule, volume to volume, and, consequently, the number of molecules and the volume they occupy will remain exactly the same after combination has taken place as it was previous to it.

We may represent this molecularly thus:



and volumetrically thus:



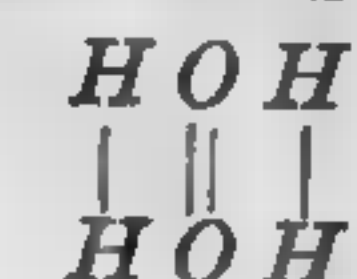
2. *Combination of a Dyad With Hydrogen.*—A dyad atom will require 2 atoms of hydrogen; 1 molecule will require 2 molecules of hydrogen; and 1 volume, 2 volumes of hydrogen; or, to express this fact in other words, dyads combine with monads in the ratio of 1 to 2.

As the resulting molecule is triatomic, it is evident that 3 diatomic molecules have combined to form 2 triatomic molecules, and that the decrease in the number of molecules also causes a corresponding decrease in volume. Thus we see that 3 volumes of simple gas give 2 volumes of compound gas, a condensation of 3 volumes to 2 volumes taking place during combination.

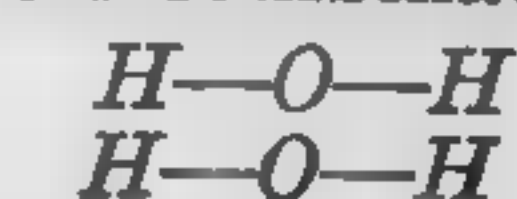
Dyads, then, combine with monads in the ratio of 1 to 2, and yield 2 volumes of the product.

ILLUSTRATION 2.—An atom of oxygen is bivalent, and its molecule diatomic. One atom of oxygen requires 2 atoms of hydrogen to form a molecule of steam, and 1 molecule of oxygen requires 2 molecules of hydrogen, and 1 volume requires 2 volumes. This may be represented molecularly thus:

Before combination



After combination



3. *Combination of a Triad With Hydrogen.*—One triad atom requires 3 monad atoms for saturation, 1 molecule requires 3 molecules, and 1 volume requires 3 volumes; since the newly produced molecule is tetratomic, the number of molecules and the corresponding volume they occupy must be reduced one-half.

Triads, then, unite with monads in the ratio of 1 to 3, yielding 2 volumes of the product.

ILLUSTRATION 3.—The trivalent atom of nitrogen, *N*, requires 3 atoms of hydrogen to form 1 molecule of ammonia.



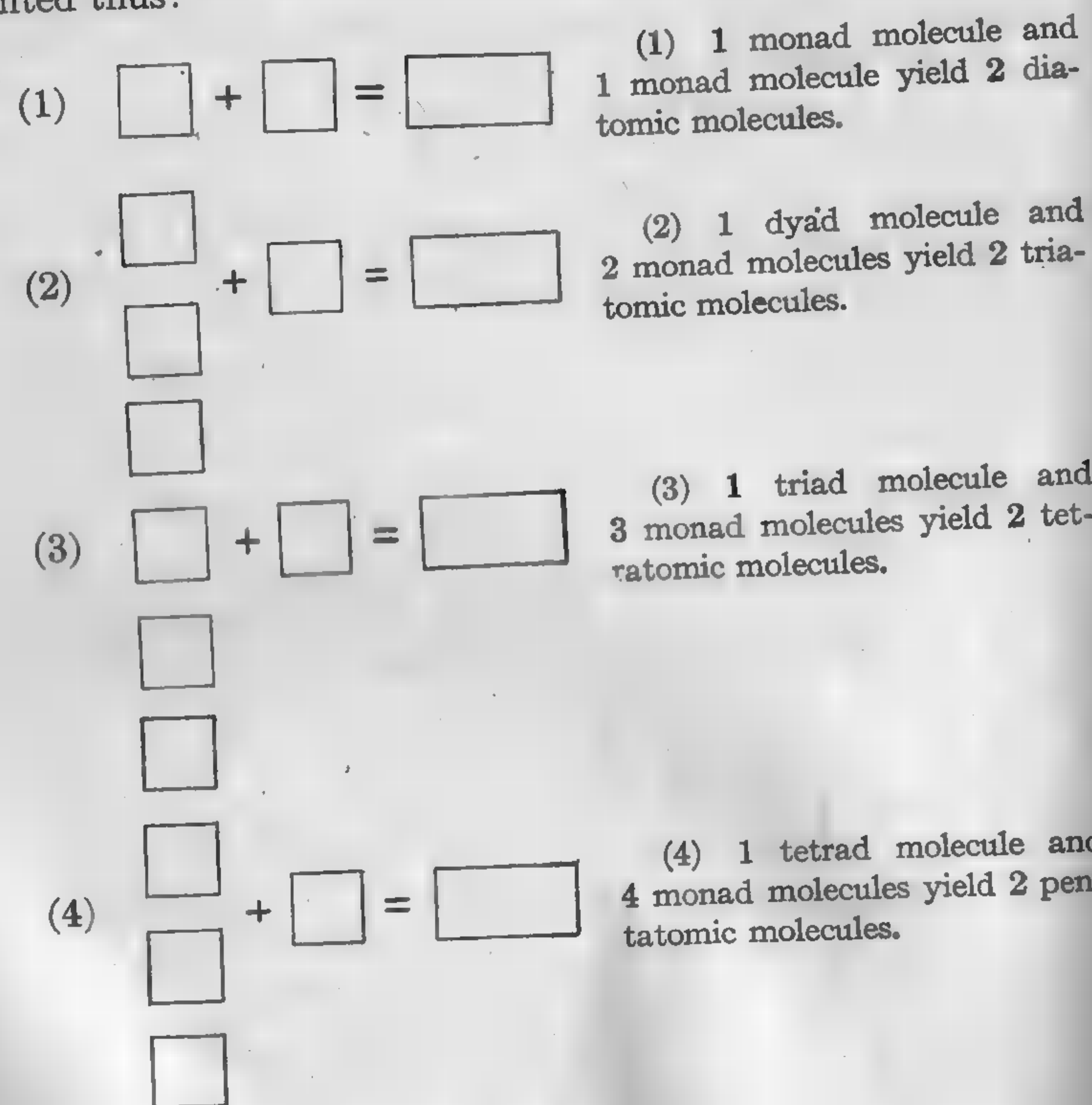
As 4 diatomic molecules yield 2 tetratomic molecules, 1 volume of nitrogen and 3 volumes of hydrogen will yield 2 volumes of ammonia gas.

4. *Combination of a Tetrad With Hydrogen.*—One tetrad atom requires 4 monad atoms for saturation; 1 tetrad mole-

cule will require 4 monad molecules, and 1 volume of any tetrad will require 4 volumes of any monad; as the resulting molecule consists of 5 atoms, the original volumes will be condensed to 2.

Tetrads, then, unite with monads in the ratio of 1 to 4 and yield 2 volumes of the product.

The preceding combinations may be graphically represented thus:



22. There are two more cases to be considered, namely, where the molecules are either monatomic or tetraatomic.

1. As all known monatomic molecules are dyads, the combination with monad atoms would be:

- 1 atom and 2 atoms give 3 atoms;
- 1 molecule and 1 molecule give 1 molecule;
- 1 volume and 1 volume give 1 volume;

or, in other words, monatomic dyad molecules combine with diatomic monad molecules in equal volume and yield 1 volume of the product.

ILLUSTRATION 1.—The monatomic dyad zinc, Zn , combines with the diatomic monad chlorine, Cl ; that is, 1 atom of zinc combines with 2 atoms of chlorine, or 1 molecule of zinc combines with 1 molecule of chlorine, or 1 volume of zinc with 1 volume of chlorine. The product is the triatomic molecule zinc chloride, $ZnCl_2$, a condensation of half the original volume taking place.

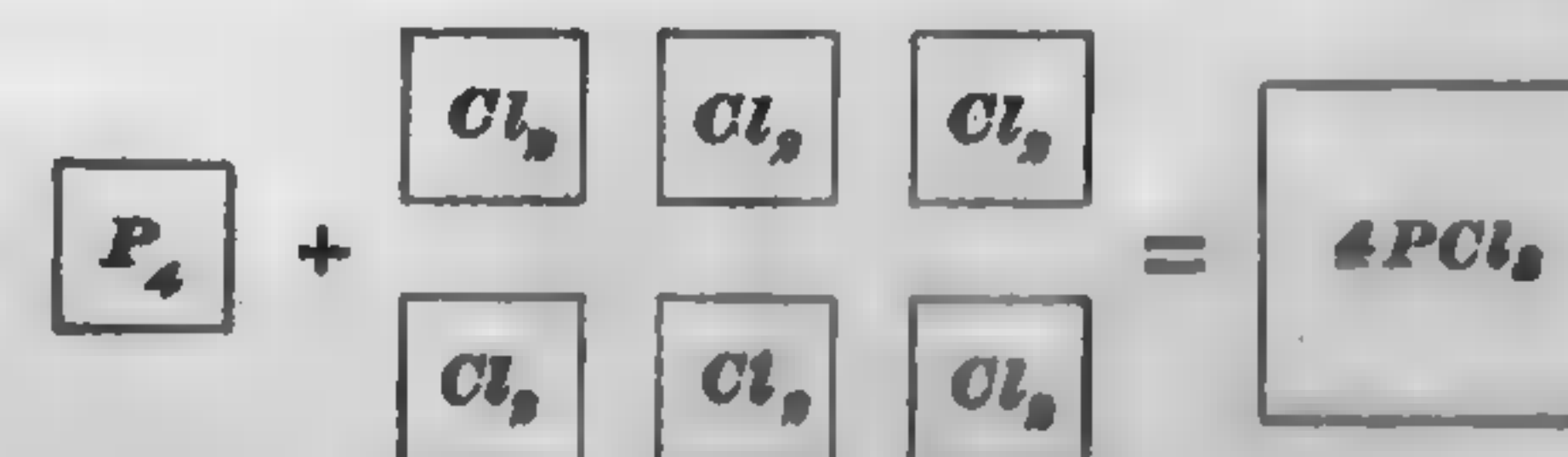
2. As all known tetraatomic molecules are triads, the atomic combination is:

1 atom and 3 atoms yield 4 atoms;

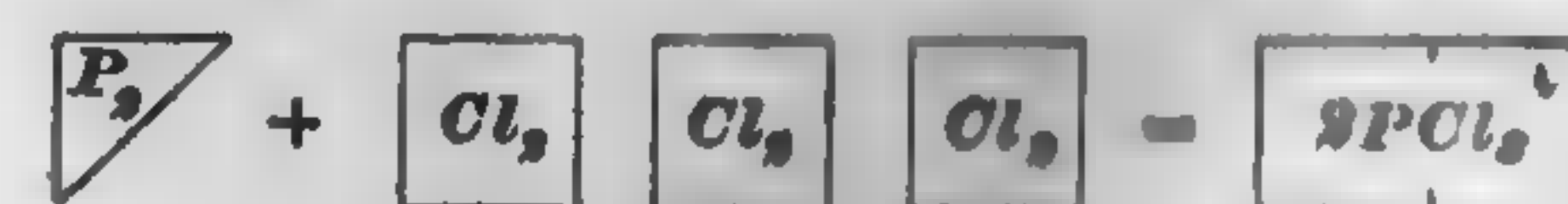
1 tetraatomic molecule and 6 diatomic molecules yield 4 tetraatomic molecules;

1 volume and 6 volumes yield 4 volumes; which means that tetraatomic triad molecules combine with diatomic monad molecules in the ratio of 1 to 6 volumes, producing 4 volumes of the product.

ILLUSTRATION 2.—Phosphorus is a triad, possessing a tetraatomic molecule. When it unites with chlorine, we have, atomically, P and Cl , giving PCl_3 , and molecularly, P_4 and $6Cl_2$, giving $4PCl_3$, or by volume:



or, as it is also sometimes graphically expressed:



CHEMICAL CALCULATIONS

REACTIONS

23. Chemical Reactions and Reagents.—The term *chemical reaction* is applied to any change that takes place in the atoms composing a molecule. The substance applied to produce the change is called a *reagent*.

Chemical reaction always occurs within the molecule. Hence, when two substances react on each other, the changes that result may be considered as taking place between single molecules; and as all molecules in homogeneous matter are alike, and what is true of one molecule must be true for any mass of them, it follows that a molecular change represents a mass change, also.

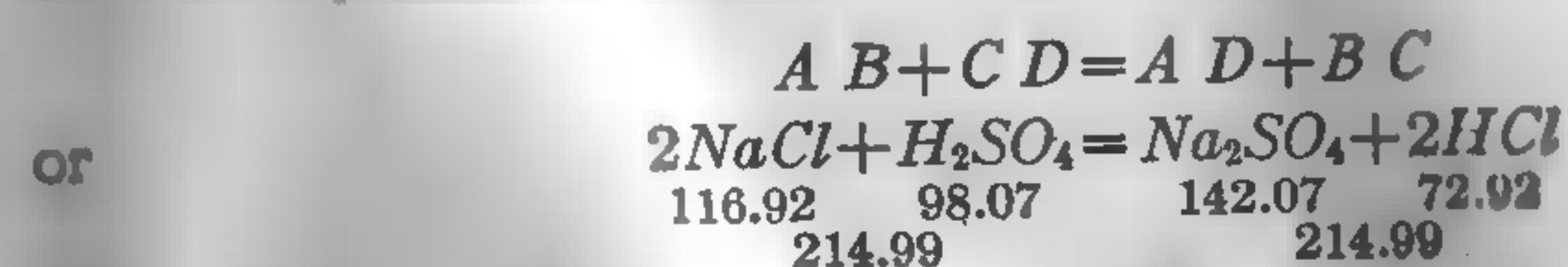
24. Chemical Equations.—Since every chemical change or reaction is simply an alteration in the association and position of atoms within the molecule, and, consequently, a change of the constitution of the molecule, this reaction may be expressed by an equation.

The substances entering into the reaction are called the *factors*; those issuing from the reaction are called the *products*.

The equation representing the reaction is written according to the following rule:

Place the formulas of the factors—connected by the sign of plus—as the first member of the equation, and the formulas of the products—also connected by the sign of plus—as the second.

ILLUSTRATION.—The reaction of the 2 molecules *A B* and *C D* would then be expressed as follows:



A chemical equation, however, not only expresses the fact of reaction, but it also indicates the quantities, by weight, concerned in it, and since the atoms remain exactly the same after the reaction as they were before, being only differently associated, it is evident that a loss of weight cannot occur through chemical reaction, and the weight of the bodies resulting from a chemical change must be the same as that of the bodies before the change, whatever it may be, had occurred.

25. Facility of Chemical Reaction.—Since a chemical reaction is the result of the reciprocal action of atoms and has for its effect a change in the composition of the molecule, it is evident that it can take place only when these atoms, and, consequently, their molecules, are brought into intimate relation. As the affinity of the atoms is only exercised at infinitely small distances, this affinity is often retarded by cohesion, which maintains the relations between molecules of solid bodies. To increase the affinity between two or more bodies it becomes necessary to diminish their cohesion. On this condition the molecules can enter within the sphere of their reciprocal attraction, and the atoms of one body can attract those of the other.

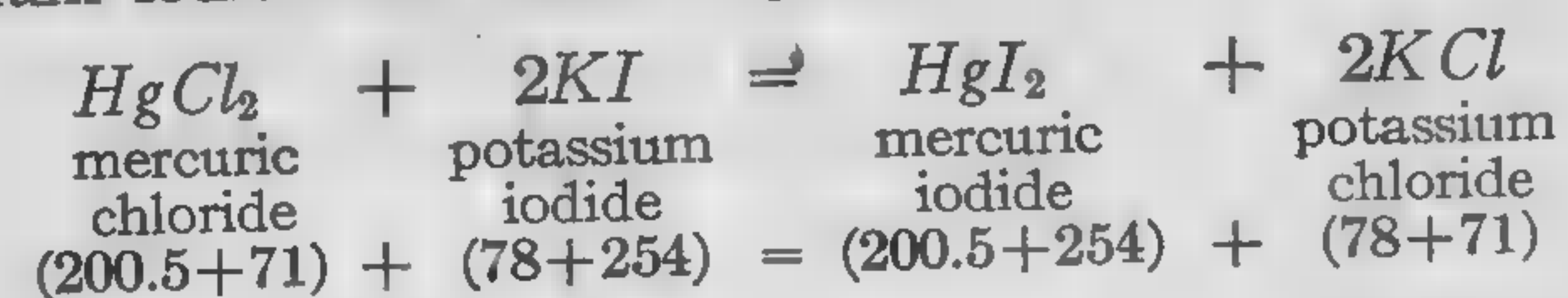
Experience teaches that this cohesion can to a certain extent be overcome and chemical reaction facilitated when the acting substances are brought into the liquid or gaseous state. Hence, either heat by which bodies are vaporized, or solution, by which bodies are liquefied, is an important aid in producing chemical reaction.

Each atom has its own weight, called its *atomic weight*, and these atomic weights are the smallest portions by weight of any simple substance—referred to the atom of hydrogen—that can take part in a chemical change.

A molecule being built up of atoms, a molecular weight is the sum of the weights of the atoms composing it.

26. Every chemical change or reaction is simply an alteration in the association and position of atoms, and all chemical equations represent such a change as occurring between definite quantities of matter.

As an example, the following equation represents the chemical action occurring when solutions of mercuric chloride and potassium iodide are mixed together.



With the assistance of a table of atomic weights, the chemist learns from this equation that one part of mercuric chloride, containing one combining proportion of mercury (weighing 200.5), and two combining proportions of chlorine (each weighing 35.5), together with two parts of potassium iodide, each containing one combining proportion of potassium (weighing 39) and one of iodine (weighing 127), together yield or produce one part of mercuric iodide, containing one combining proportion of mercury (weighing 200.5) and two of iodine (weighing 127 each), and two parts of potassium chloride, each consisting of one combining proportion of potassium (weighing 39) and one of chlorine (weighing 35.5)*. As no chemical change affects the weight of matter, the weight of the quantity of a compound represented by its formula must be the sum of those of the constituent atoms; so, too, the weight of the bodies resulting from a chemical change must be the same as that of the bodies before the change, whatever it may be, had occurred; hence, the sum of the atomic weights on one side of the equality sign must equal the sum of the atomic weights on the other side of the equality sign, otherwise there will be no true equation. Also, the same number of combining proportions of each element must appear on each side of the equation, else the reaction will not equate. In the instance just given, it will be noticed that there are the same number of atoms of the elements *Hg*, *Cl*, *K*, and *I* on one side of the equality sign as on the other, and that therefore the equation is perfect. Although, given a chemical equation and table of combining weights, it is possible to state what relative weight of each element is concerned in

* In order to facilitate calculations, where great exactness is not required, it is customary to use approximate atomic weights.

any chemical action, it must never be forgotten that such weights are always determined by chemical analysis, and that from the data thus obtained the equation is compiled. So, too, the series of combining weights is simply a tabular expression of results obtained by practical analytic investigation.

27. To Find Percentage Composition.—Knowing the molecular weight of any substance, the number of atoms it contains, and the atomic weight of each constituent atom, the percentage composition (that is, the composition of 100 parts of a substance), the form in which results of analyses are usually expressed, can easily be found by the following rule:

Rule.—Multiply the atomic weight by the number of atoms, and divide by the molecular weight of the compound; the quotient multiplied by 100 will be the percentage amount of that constituent.

EXAMPLE 1.—The formula for potassium chlorate is KClO_3 ; what is the percentage quantity of each element in the compound?

SOLUTION.—Assign to each atom its weight; then,

$$\begin{array}{ccccccc} \text{K} & + & \text{Cl} & + & \text{O}_3 & = & \text{KClO}_3 \\ 39 & & 35.5 & & (16 \times 3) & & 122.5 \end{array}$$

which means that 122.5, being the sum of the constituent atoms, represents the molecular weight of potassium chlorate, and that 122.5 parts of KClO_3 contain 39 parts of potassium, 35.5 parts of chlorine, and 48 parts of oxygen. Now, multiplying each atomic weight by the number of atoms, dividing by the molecular weight, and multiplying the quotient by 100, the result is:

$$\text{Oxygen} = \frac{16 \times 3}{122.5} = .3918 \times 100 = 39.18 \text{ per cent. Ans.}$$

$$\text{Chlorine} = \frac{35.5 \times 1}{122.5} = .2898 \times 100 = 28.98 \text{ per cent. Ans.}$$

$$\text{Potassium} = \frac{39 \times 1}{122.5} = .3184 \times 100 = 31.84 \text{ per cent. Ans.}$$

Total, 100.00 per cent.

EXAMPLE 2.—The mineral hematite has the formula Fe_2O_3 ; what percentage of metallic iron does it contain?

$$\begin{array}{rcl} \text{SOLUTION.} & & \text{Fe}_2 = 56 \times 2 = 112 \\ & & \text{O}_3 = 16 \times 3 = 48 \\ & & \hline & & 160 \end{array}$$

$$\text{Iron} = \frac{56 \times 2}{160} = .70 \times 100 = 70 \text{ per cent. Ans.}$$

EXAMPLE 3.—What percentage of copper is there in the mineral having the formula $CuFeS_2$?

SOLUTION.—

$$\begin{array}{rcl} Cu & = 63.5 \times 1 & = 63.5 \\ Fe & = 56 \times 1 & = 56.0 \\ S_2 & = 32 \times 2 & = 64.0 \\ & & \hline & & 183.5 \end{array}$$

$$\text{Copper} = \frac{63.5 \times 1}{183.5} = .346 \times 100 = 34.6 \text{ per cent. Ans.}$$

28. To Find the Formula of a Compound.—To find the number of atoms of the constituents of a compound, or, in other words, the chemical formula of the molecule, proceed according to the following rule:

Rule.—Divide the percentage amount of each element present by the atomic weight of that element; take the smallest of the values so obtained as unity and divide the remaining numbers by it; the quotients then represent the ratios of the number of atoms of each element present to each other.

EXAMPLE 1.—The percentage composition of sulphuric acid is: hydrogen, 2.04 per cent.; sulphur, 32.65 per cent.; and oxygen, 65.31 per cent. What is the formula of sulphuric acid?

SOLUTION.—The atomic weights of hydrogen, sulphur, and oxygen are, respectively, 1, 32, and 16. Hence,

$$\begin{array}{rcl} \text{Hydrogen} & = 2.04 \div 1 & = 2.04 \\ \text{Sulphur} & = 32.65 \div 32 & = 1.02 \\ \text{Oxygen} & = 65.31 \div 16 & = 4.08 \end{array}$$

Now, dividing by the smallest number, the relation of the atoms becomes: Sulphur, 1; hydrogen, 2; and oxygen 4. Therefore, the formula of sulphuric acid is H_2SO_4 . Ans.

EXAMPLE 2.—Potassium cyanide has the following composition: Potassium, 60.04 per cent.; carbon, 18.41 per cent.; and nitrogen, 21.5 per cent. What is its formula?

SOLUTION.—

$$\begin{array}{rcl} \text{Potassium} & = 60.04 \div 39 & = 1.53 \\ \text{Carbon} & = 18.41 \div 12 & = 1.53 \\ \text{Nitrogen} & = 21.5 \div 14 & = 1.52 \end{array}$$

Now, dividing by the smallest number, the values $K=1$, $C=1$, and $N=1$ are obtained; hence, the formula of potassium cyanide is KCN . Ans.

29. Calculation of an Atomic Group.—It is frequently necessary to calculate the percentage of a group of atoms

in a molecule. This is calculated in exactly the same way as the percentage of a constituent of a compound, but a few examples will render the calculation clearer.

EXAMPLE 1.—The mineral magnesite, $MgCO_3$, is decomposed by heat into MgO and CO_2 ; how much magnesium oxide, MgO , is there in 100 parts of magnesite?

SOLUTION.—The molecular weight of MgO is 40, and of $MgCO_3$ is 84. hence,

$$40 \div 84 = .4762 \times 100 = 47.62\% \text{ } MgO. \text{ Ans.}$$

EXAMPLE 2.—What percentage of carbon dioxide, CO_2 , is there in the mineral siderite, $FeCO_3$?

SOLUTION.—The molecular weight of $FeCO_3$ is 116, and of CO_2 is 44; hence,

$$44 \div 116 = .3793 \times 100 = 37.93\% \text{ } CO_2. \text{ Ans.}$$

EXAMPLE 3.—What percentage of potassium chloride is there in potassium platonic chloride, K_2PtCl_6 ?

SOLUTION.—As the molecule of K_2PtCl_6 is made up of $2KCl \cdot PtCl_4$, the molecular weight of the potassium chloride present is twice the molecular weight of KCl , or $74.5 \times 2 = 149$. The molecular weight of K_2PtCl_6 is 486; hence,

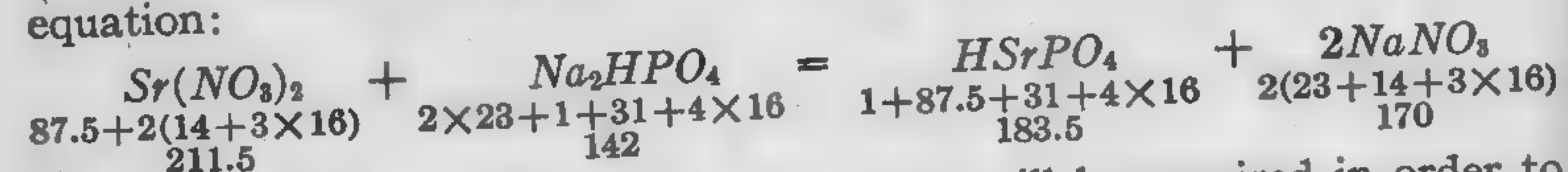
$$149 \div 486 = .3065 \times 100 = 30.65\% \text{ } KCl. \text{ Ans.}$$

30. Calculations From Equations.—Simple arithmetical principles apply in calculating the weights of substances that enter into or are produced by chemical changes. In these calculations three facts must always be remembered: (1) that the atomic weight of an element is a constant quantity; (2) that the same chemical substance is always composed of the same elements in the same proportions; (3) that a chemical equation always represents the results of a chemical action. In an equation there must always be the same number of atoms, of each element entering into the reaction on both sides of the equation, and consequently each side of the equation will represent the same weight of matter.

In calculating the results of a chemical reaction, the equation representing it must first be written and completed. The molecular weights of the compounds or elements taking part must be calculated from a table of atomic weights and placed below the formulas. If these facts are remembered it will

be easily seen that the proportions represented by an equation are true for any weight. Again, knowing the equation representing a reaction, and the weight of one of the substances entering into the reaction, then the amount of any substance produced in the reaction, or the amount of any substance taking part in it, can be readily calculated.

EXAMPLE 1.—Sodium nitrate is prepared by the action of disodium hydrogen phosphate on strontium nitrate, according to the following equation:

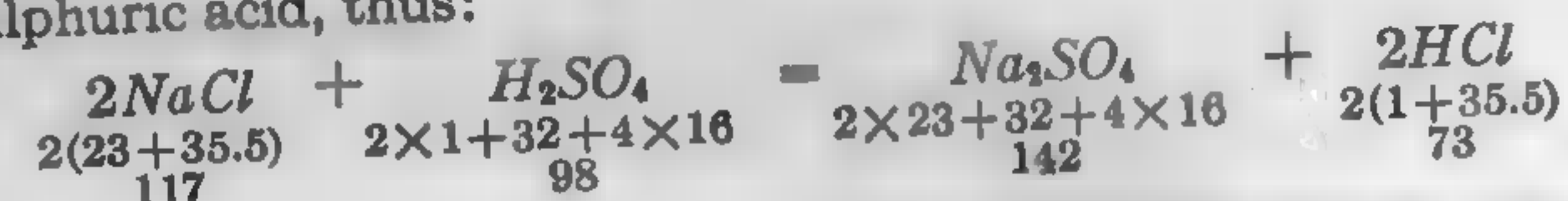


How much disodium hydrogen phosphate will be required in order to yield 309 grams of sodium nitrate?

SOLUTION.—Since 142 grams of disodium hydrogen phosphate yield 170 grams of sodium nitrate, it will require x grams of disodium hydrogen phosphate to yield 309 grams of sodium nitrate. Hence, putting this in the form of a proportion, the result is

$$142 : 170 = x : 309. \quad x = 258.1 \text{ grams. Ans.}$$

EXAMPLE 2.—Sodium sulphate is formed by treating sodium chloride with sulphuric acid, thus:



(a) How much sodium chloride will be required to furnish 100 pounds of sodium sulphate? (b) How many pounds of sulphuric acid will be required?

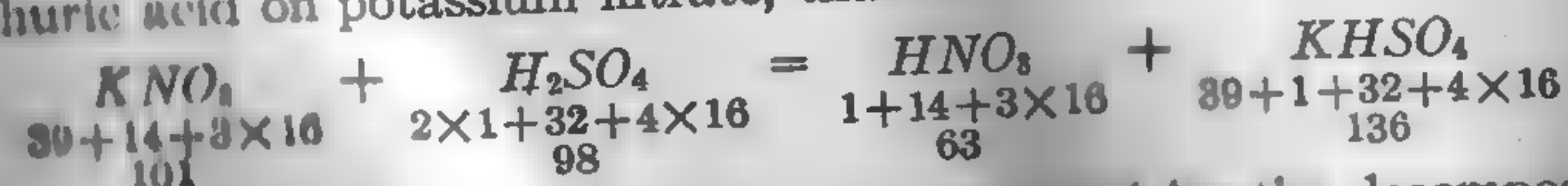
SOLUTION.—(a) 117 pounds of sodium chloride yield 142 pounds of sodium sulphate; therefore, x pounds of sodium chloride will yield 100 pounds of sodium sulphate. In the form of a proportion this is:

$$117 : 142 = x : 100. \quad x = 82.4 \text{ pounds. Ans.}$$

(b) 98 pounds of sulphuric acid are required for 142 pounds of sodium sulphate; hence,

$$98 : 142 = x : 100. \quad x = 69 \text{ pounds. Ans.}$$

EXAMPLE 3.—Potassium acid sulphate is produced by the action of sulphuric acid on potassium nitrate, thus:

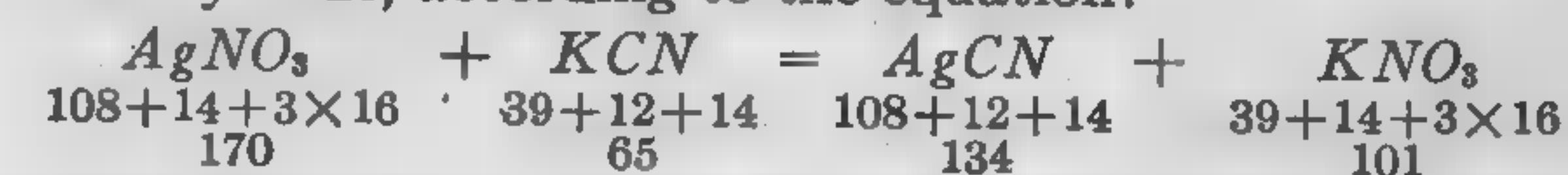


How much potassium acid sulphate is produced by the decomposition of 500 grams of potassium nitrate by sulphuric acid?

SOLUTION.—101 grams KNO_3 yield 136 grams KHSO_4 ; therefore, 500 grams KNO_3 will yield x grams KHSO_4 . In the form of a proportion this becomes

$$101 : 136 = 500 : x. \quad x = 673.27 \text{ grams. Ans.}$$

EXAMPLE 4.—Silver cyanide is produced by the action of silver nitrate on potassium cyanide, according to the equation:



How much potassium nitrate is yielded by the decomposition of 100 grams of silver nitrate by potassium cyanide?

SOLUTION.—101 grams of KNO_3 are obtained by the decomposition of 170 grams of AgNO_3 , so 100 grams of AgNO_3 will yield x grams KNO_3 . Hence, the proportion:

$$170 : 101 = 100 : x. \quad x = 59.4 \text{ grams. Ans.}$$

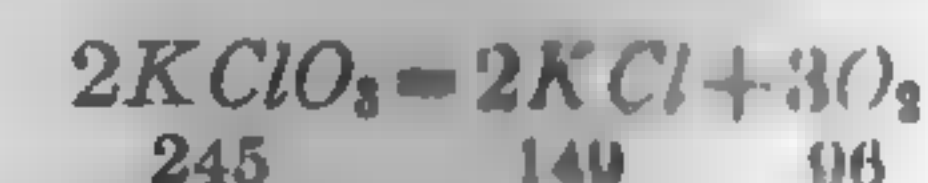
31. It frequently happens that the product of a reaction is a gas, and as the volume of a gas varies with the changes in the temperature and pressure these factors must be taken into consideration. As this is very important a few examples will be given.

32. To Find the Volume of Gaseous Product.—The volume of a gaseous product must always be determined first at normal temperature and pressure and then changed to the volume at the existing temperature and pressure. The weight of the gas can be obtained by the methods already given and is then corrected according to the following examples:

Case I.—To find the volume of gaseous product at normal temperature and pressure.

EXAMPLE.—What volume of oxygen gas at normal temperature and pressure can be obtained from 30 grams of potassium chlorate?

SOLUTION.—When potassium chlorate is heated, oxygen is evolved according to the equation:



By the methods given in the preceding pages the proportion $245 : 30 = 96 : x$ is obtained, from which x equals 11.75 grams of oxygen.

As 1.429 grams of oxygen occupies 1 liter of space, the space occupied by 11.75 grams is obtained by dividing this weight by the weight of 1 liter, or $11.75 \div 1.429 = 8.22 +$ liters of oxygen. Ans.

Case II.—To find the volume of gaseous product at other than normal temperature, the pressure remaining normal.

EXAMPLE.—How many liters of oxygen at 20° C. and normal pressure can be obtained from 30 grams of potassium chlorate?

SOLUTION.—From the preceding problem it is found that 8.22 liters of oxygen are obtained, at normal temperature and pressure, from 30 grams of potassium chlorate. But, as the temperature of this gas is now 20° C., it is 20° above normal, and consequently occupies more space than it would at 0° (normal temperature). Now in *Inorganic Chemistry*, Part 1,

$$V' = \frac{V(273+t)}{273}, \text{ or } V' : V = T' : T$$

Now, substituting the proper values,

$$V' = \frac{8.22 \times (273+20)}{273} = 8.82 \text{ liters. Ans.}$$

Case III.—To find the volume of gaseous product at other than normal pressure, the temperature remaining normal.

EXAMPLE.—What volume of oxygen, at 0° and 700 mm. pressure, can be obtained from 30 grams of potassium chlorate?

SOLUTION.—In Case I it was found that 8.22 liters of oxygen was obtained at normal temperature and pressure. In this case, however, the pressure is less than normal, and hence the volume will be greater than at normal pressure; and as the volume varies inversely as the pressure, the proportion is

$$V : V' = P' : P$$

hence, substituting the proper values,

$$8.22 : V' = 700 : 760$$

or

$$V' = \frac{8.22 \times 760}{700} = 8.92 \text{ liters. Ans.}$$

Sometimes it becomes necessary to correct the volume of a gas for both temperature and pressure at the same time. This can, of course, be performed by correcting the volume for one factor, and then by using the corrected volume as the starting point correct for the other factor. By combining the two formulas for the correction of volume, the same end can be reached by one operation by means of the following formula:

$$V' = \frac{T'PV}{TP'}$$

in which V' = new volume;
 V = old volume;
 T' = new absolute temperature (273 + t);
 T = old absolute temperature (273 + t);
 P' = new pressure;
 P = old pressure.

It sometimes becomes necessary to convert a volume of gas into its weight in grams, or to change the weight in grams into volume in liters or fraction of a liter. This is done by multiplying the volume in liters by the weight of 1 liter, or by dividing the weight of the gas by the weight of 1 liter.

EXAMPLE 1.—50 liters of hydrogen measured at 0° C. and 760 mm. will weigh how many grams?

SOLUTION.—1 liter of hydrogen weighs .089873 gram; therefore, 50 liters of hydrogen will weigh

$$50 \times .089873 = 4.49 + \text{grams. Ans.}$$

EXAMPLE 2.—What volume will 6.1632 grams of hydrogen occupy at 0° C. and 760 mm.?

SOLUTION.—1 liter of hydrogen weighs .089873 gram at 0° C. and 760 mm.; hence, 6.1632 grams of hydrogen will occupy

$$6.1632 \div .089873 \text{ or } 68.5766 \text{ liters. Ans.}$$

EXAMPLES FOR PRACTICE

- Find the percentage composition of $KHSO_4$.
 Ans. $\begin{cases} K = 28.67\% \\ H = 0.74\% \\ S = 23.53\% \\ O = 47.06\% \end{cases}$
- The formula of calcium chloride is $CaCl_2$; what percentage of calcium and chlorine will be found in 100 parts of calcium chloride?
 Ans. $\begin{cases} Ca = 36\% \\ Cl = 64\% \end{cases}$
- Borax, when dried, has the formula $Na_2B_4O_7$. What is its percentage composition?
 Ans. $\begin{cases} Na = 22.77\% \\ B = 21.78\% \\ O = 55.45\% \end{cases}$
- Anhydrous sodium carbonate contains 43.4 per cent. sodium, 11.32 per cent. carbon, and 45.28 per cent. oxygen. What is the formula of sodium carbonate?
 Ans. Na_2CO_3

5. Silver nitrite has the following composition: Silver, 70.13 per cent.; oxygen, 20.77 per cent.; and nitrogen, 9.09 per cent. Calculate the formula of silver nitrate from these figures. Ans. $AgNO_3$

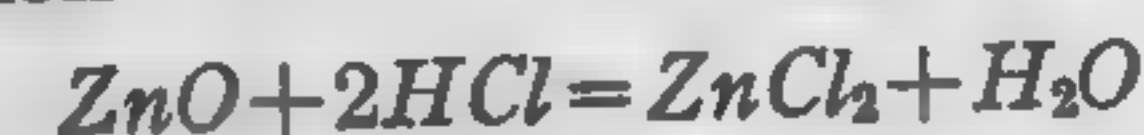
6. Calcium carbonate is decomposed into CaO and CO_2 by heat. Determine the percentage of CaO in 100 parts of $CaCO_3$. Ans. $CaO = 56\%$

7. A determination of the silver in a compound yields a certain amount of $AgCl$. What percentage of silver is there in the chloride? Ans. 75.26%

8. Arsenic is determined as $Mg_2As_2O_7$; what percentage of As_2O_3 is present in $Mg_2As_2O_7$? Ans. 63.87%

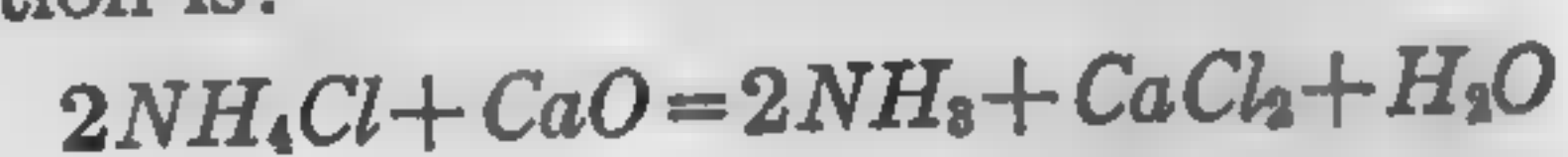
9. Sulphur is precipitated and weighed as $BaSO_4$; determine the percentage of SO_3 in $BaSO_4$. Ans. 34.33%

10. Zinc oxide treated with hydrochloric acid yields zinc chloride, according to the equation



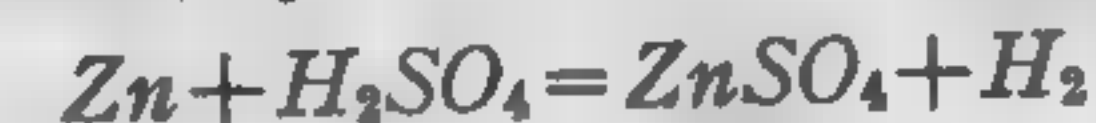
(a) Calculate the weight of hydrochloric acid necessary to form 150 grams of zinc chloride. (b) How many grams of zinc oxide will be required by 100 grams of hydrochloric acid? Ans. (a) 80.51 gr. (b) 110.96 gr.

11. How many pounds of lime, CaO , are required to liberate 30 pounds of ammonia, NH_3 , from ammonium chloride, NH_4Cl ? The equation representing the reaction is:



Ans. 49.41 lb.

12. Hydrogen is formed by the action of sulphuric acid on zinc; thus.



(a) What amount of $ZnSO_4$ is formed when 15 grams of zinc are treated with sulphuric acid? Ans. 37.15 gr.

(b) How much zinc is required to form zinc sulphate with 20 grams of sulphuric acid? Ans. 13.26 gr.

(c) How many liters of hydrogen are formed at $0^\circ C.$ and 760 mm. pressure when 45 grams of zinc are treated with sulphuric acid? Ans. 15.41 liters

(d) What volume of hydrogen is formed in (c) at $12^\circ C.$ and 754 mm. pressure? Ans. 16.21 liters

THERMOCHEMISTRY

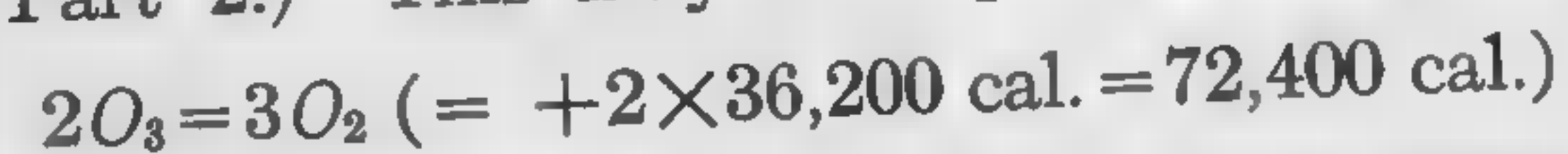
33. It was stated that whenever chemical combination takes place it is accompanied by either an evolution or absorption of heat. In most cases heat is evolved, though this is not universally the case. In studying the subject of oxidation, it was seen that the amount of heat evolved during the oxidation of the combustible portions of a tree was the same whether the oxidation proceeded rapidly or slowly. This is universally true. That is, whenever a chemical change takes place, a certain definite amount of heat is either evolved or absorbed. The study of the heat relations connected with chemical changes is known as **thermochemistry**. When this subject is more thoroughly developed, so that the heat relations of reactions are more thoroughly understood, it will probably be of considerable importance. Indeed, with our present knowledge, it is of considerable assistance in dealing with certain classes of problems.

Thermochemical reactions are of two kinds, *exothermic* and *endothermic*. **Exothermic** reactions are reactions in which heat is liberated. **Endothermic** reactions are reactions in which heat is absorbed. Reactions that evolve heat usually take place readily; those that absorb heat must have the heat supplied from without, in order that the reaction may proceed.

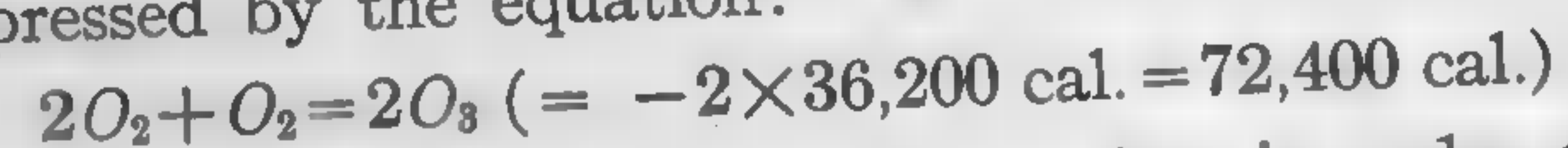
Exothermic compounds—that is, compounds formed by reactions that evolve heat—are more stable than those formed by endothermic reactions; for, in order to decompose an exothermic compound, it is necessary to supply the same amount of heat that was given off during its formation. From this fact it naturally follows that the greater the amount of heat evolved in the formation of an exothermic compound, the more stable the compound will be. On the other hand, endothermic compounds are decomposed with the evolution of heat. They are unstable and are often explosive. This may be explained in the language of physics by saying that endother-

mic compounds have more energy than exothermic compounds. This subject will be rendered more clear by the study of a few individual cases.

34. Thermochemical Relations of Oxygen.—It has been stated that ozone readily breaks down into oxygen, and during this breaking down considerable heat is evolved. Careful measurements have shown that when 2 gram-molecules (the molecular weight taken in grams) of ozone break down into ordinary oxygen, 72,400 calories are evolved. (See *Physics*, Part 2.) This may be expressed by the equation:



As this heat is given off during the breaking down of ozone, it is evident that an equivalent amount of energy must be supplied from outside in order to produce ozone. This may be expressed by the equation:

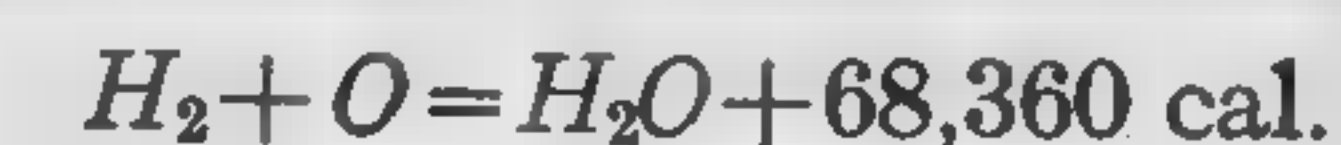


From these equations—which show that in order to prepare ozone from oxygen it is necessary to supply heat to carry on the reaction; whereas, in breaking down into common oxygen the ozone generates more heat than is needed to carry on the reaction—it is evident that the common oxygen is more stable than ozone. This may be partly expressed by saying that the ozone contains more energy and consequently reacts more energetically.

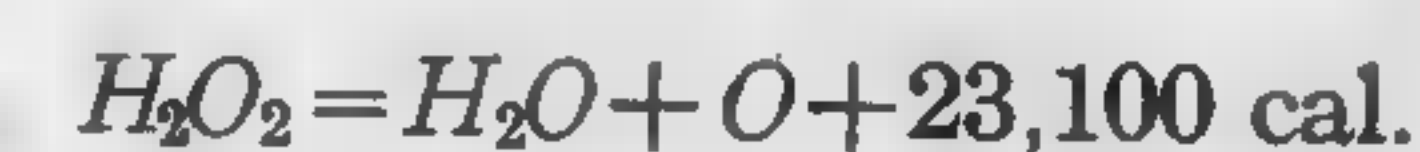
In stating the quantities of heat evolved or absorbed, these quantities do not refer to 1 gram of the reacting substances, but to the weights stated in grams corresponding to the atomic weights of the elements entering into combination. Thus, the equation, $2O_3 = 3O_2 + 72,400$ calories, means that when 96 grams of ozone are decomposed into common oxygen, 72,400 calories of heat are evolved.

35. Thermochemical Relation of Hydrogen.—When hydrogen burns in air or oxygen, a great deal of heat is evolved. This is usually expressed by saying that hydrogen burns with an exceedingly hot flame. When 1 gram of hydrogen burns in air or oxygen, 34,180 calories are evolved, or

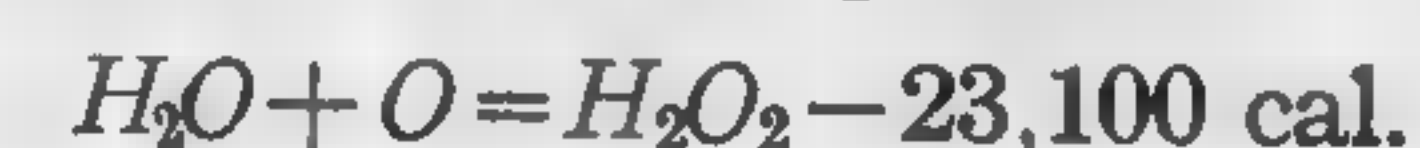
when 2 grams of hydrogen unite with 16 grams of oxygen, 68,360 calories are evolved. This is expressed by the equation:



When hydrogen peroxide decomposes into water and oxygen, 23,100 calories are evolved, as expressed by the equation:



Consequently, this same amount of heat is required to accomplish the formation of the peroxide:



Therefore, in order to obtain the peroxide, this amount of energy must be supplied to support the reaction. When hydrochloric acid acts on barium dioxide, more than this amount of heat is evolved, and consequently the heat necessary for the formation of the peroxide is generated during the reaction and supplied as needed, so that the formation in this way is possible.

36. Summary.—In many cases the thermochemical relations are important and throw much light on chemical reactions, but if all the conditions were understood and the quantities capable of measurement, the knowledge of thermochemical relations would be of much greater value. For instance, if a mass of hydrogen and a mass of oxygen each consisted of isolated atoms at rest, and after combination, if the molecules of the product as well as their constituent atoms were at rest, the heat evolved during combination would be a direct measure of the affinity of hydrogen and oxygen for each other. It is known that neither hydrogen nor oxygen consists of isolated atoms, and probably none of the other conditions mentioned exists. It is certain that energy is required to decompose the molecules of hydrogen and oxygen into uncombined atoms, and assuming that the intramolecular energy of the product of the combustion of these gases is the same as the energy of the gases, the heat generated during their combination would be the difference between the heat generated during combination and the heat used to decompose the molecules into atoms. This can hardly

be assumed, however, for there is no evidence that the intramolecular energy of water is the same as that of the gases that compose it. Though our knowledge of thermochemical relations is very incomplete, still thermochemistry is of some importance even in its present undeveloped state, and consequently some attention will be given to the subject in these Sections.

CRYSTALLOGRAPHY

37. Although crystallography is not properly a part of chemistry, some knowledge of this subject is of such importance to the chemist that it will be briefly treated at this point.

Most chemical substances, when they pass from the liquid or gaseous into the solid state, assume some definite geometric form, or are said to *crystallize*. Crystals are produced when a substance, such as potassium nitrate, is dissolved in water and the solution is allowed to gradually evaporate; when a body, such as sulphur, is melted and allowed to solidify by cooling; or when a volatile substance, such as iodine, is vaporized, and the vapor condensed on a cool surface.

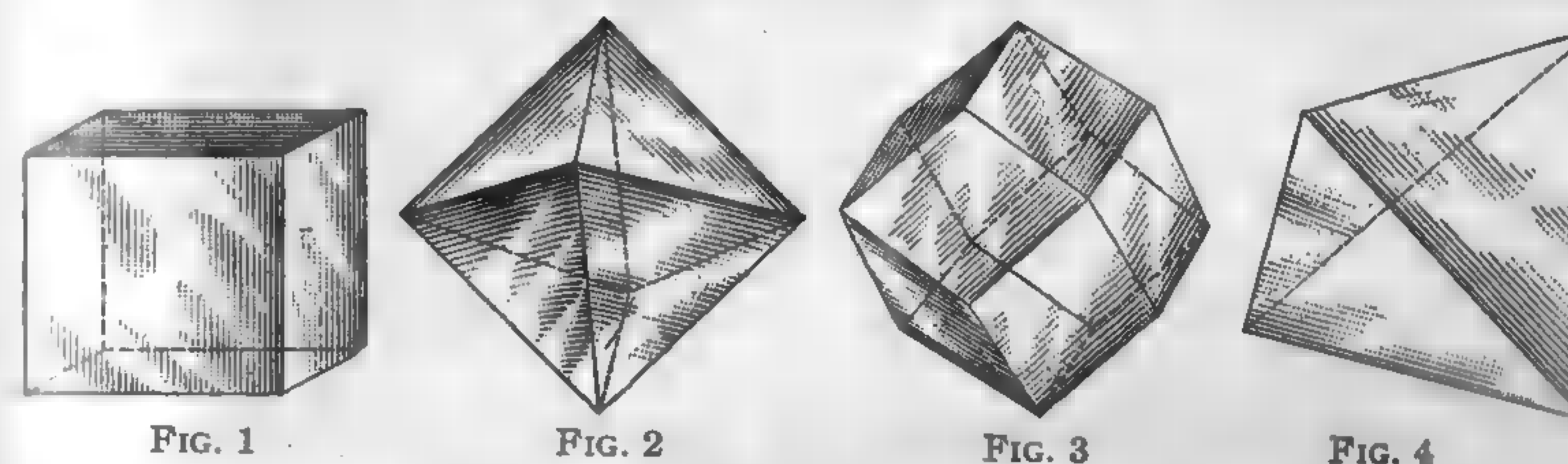
When a solution will dissolve no more of the solid, at a given temperature, the solution is *saturated*. If, however, the solution is boiled in a flask the solution will generally dissolve some more of the solid and become *supersaturated*. If a small crystal of the solid is dropped into a supersaturated solution, crystallization will immediately begin and will continue until the point of saturation is reached.

Many native minerals exhibit perfect crystalline forms, though investigations have not yet disclosed the process of their formation. Judging from their perfect shape the assumption is justified that the process of their formation must have been a necessarily slow one. Besides their regular shape, these crystalline bodies possess other remarkable properties, that is, a peculiar power of splitting in certain directions more readily than in others, a property that is known as *cleavage*; and in many cases they possess the property of allow-

ing light to pass more readily in certain directions than in others, giving rise to the well-known phenomena of *double refraction*.

A body assuming two distinct crystalline forms is said to be *dimorphous*; the study of even the more familiar elements includes some very important instances of dimorphism. A body that does not occur in crystals is termed *amorphous*; that is, without crystalline form. Certain complicated structures of the vegetable and animal world exhibit a structure that, although non-crystalline, is not devoid of a certain definite arrangement, and to which the name *organized*, or *cellular structure* has been given. A substance, however, may have both a crystalline and an amorphous variety.

As a rule, every particular substance possesses a definite form, in which it will always crystallize, and by which it may



be distinguished; when a crystal is formed from aqueous solution, for instance, the most minute particle possesses the same crystalline structure and perfect form as the largest crystals.

Certain substances exhibiting a similarity in their chemical constitution are found to crystallize in the same forms; these are said to be *isomorphous*.

38. *System of Crystallization*.—Many thousands of crystal forms are known, but they can all be referred to six classes or systems. This can be accomplished by comparing the crystals according to their directions of development, called axes, that is, we imagine a series of lines (axes) passing through the middle points of the crystals, so placed that the crystal faces lie symmetrically about the axes. From the number of axes, their length and inclination, all crystals can be classified into six systems:

1. *Regular or Isometric System*.—Three axes of equal length, all at right angles to one another. The simple forms of this system are the *cube*, Fig. 1; the *regular octahedron*, Fig. 2; the *rhombic dodecahedron*, Fig. 3; and the *regular tetrahedron*, Fig. 4.

The following are examples of substances crystallizing in this system: common salt, diamond, alum, iron pyrites, garnet, fluorspar, etc.

2. *Quadratic or Tetragonal System*.—Three axes, two of equal length, the third (principal axis) longer or shorter, all at right angles to one another.

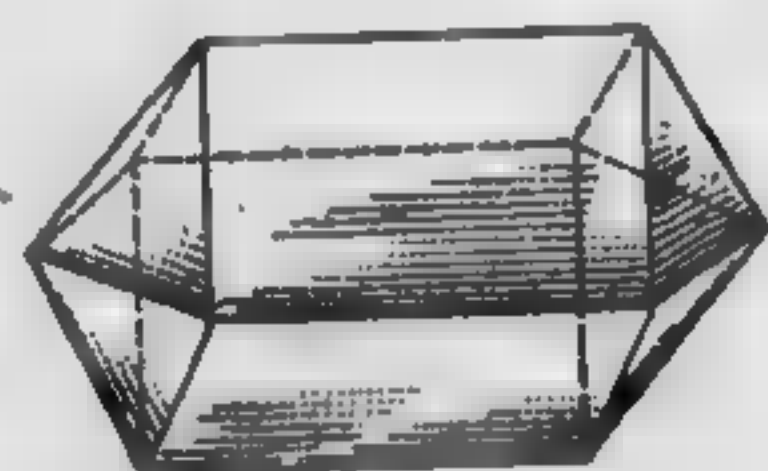


FIG. 5

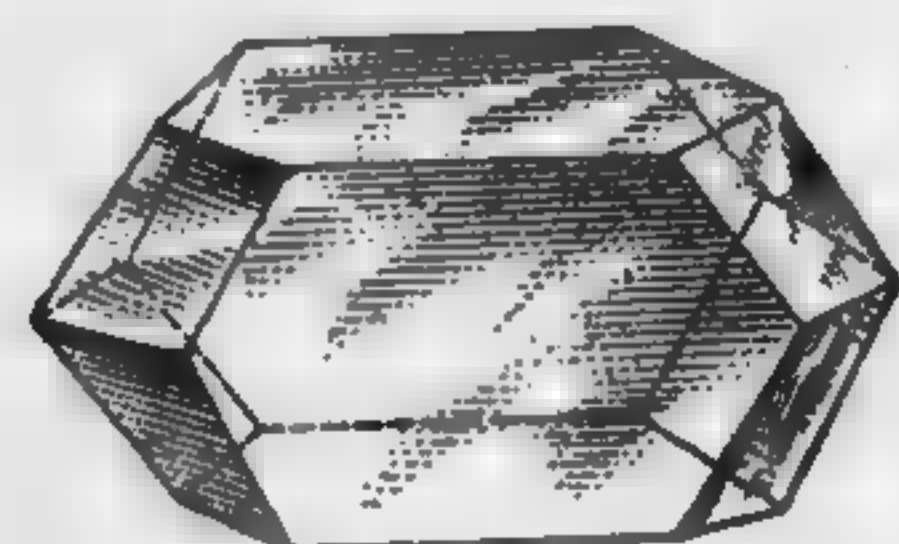


FIG. 6

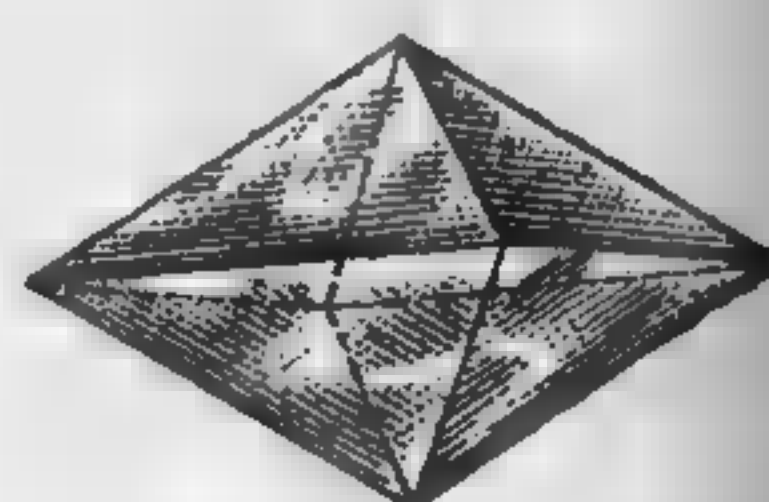


FIG. 7

The simple forms of this system are the *first right square prism*, Fig. 5; the *second right square prism*, Fig. 6; the *first right square octahedron*, Fig. 7; and the *second right square octahedron*, Fig. 8.

In the first square prism, the axes terminate in the center of each of the sides, and in the second square prism, the axes terminate at the intersection of the sides; this is reversed in the octahedron.

The following are examples of substances crystallizing in this system: stannic oxide, copper pyrites, yellow prussiate of potash, etc.

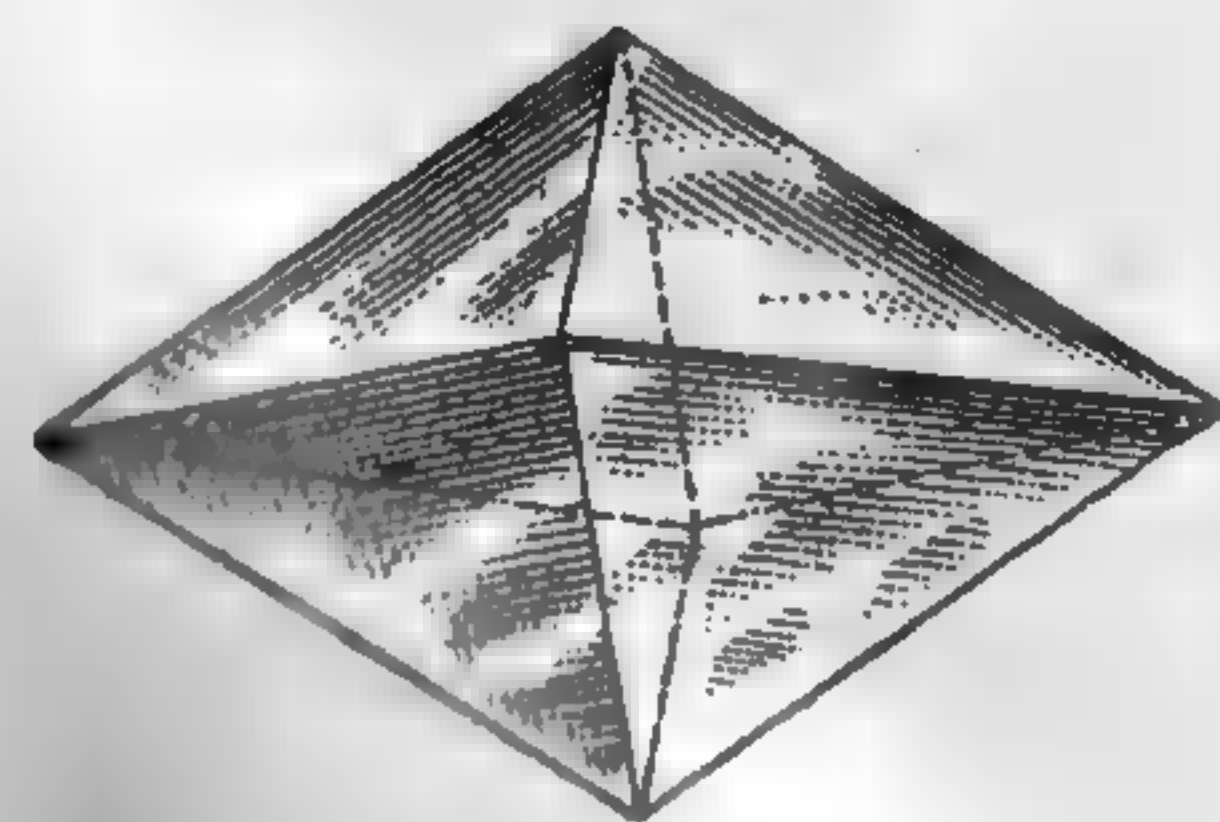


FIG. 8

the *right rhombic prism*, Fig. 11.

Examples of this class are: native sulphur, calcium sulphate, barium sulphate, magnesium sulphate, calcium carbonate, potassium nitrate, etc.

4. *Monoclinic, Monosymmetric, or Clinorhombic System*. Three axes of different lengths, two of these at an oblique

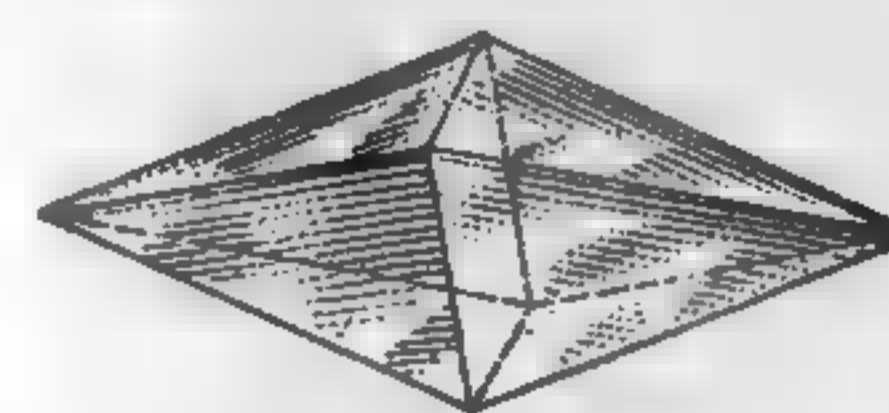


FIG. 9

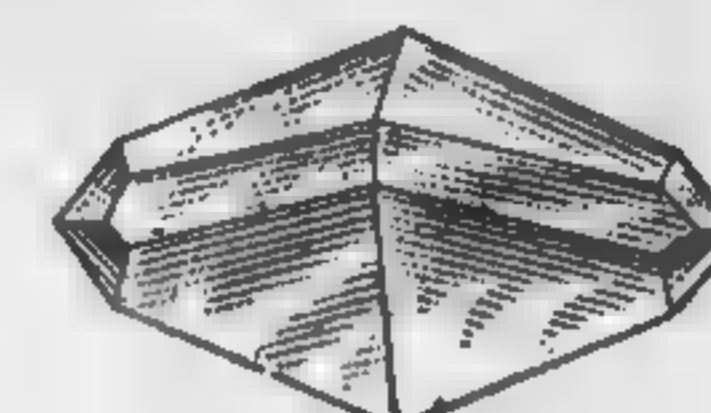


FIG. 10

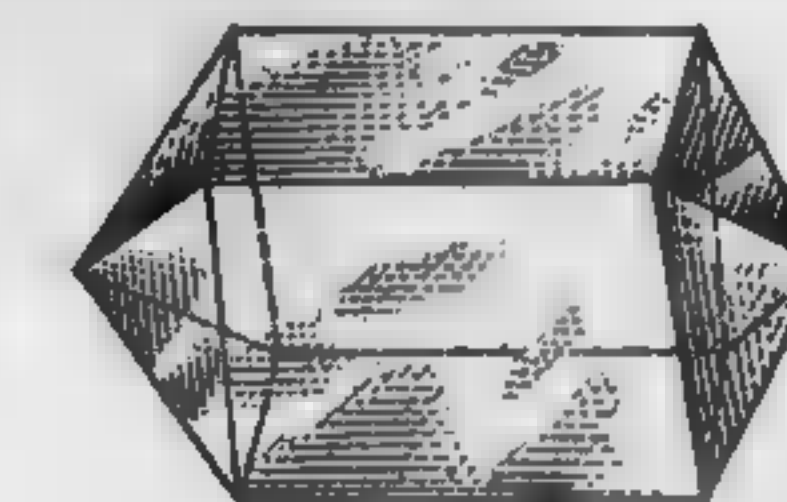


FIG. 11

angle with one another, but at right angles to the third. The *oblique rhombic octahedron*, Fig. 12, belongs to this system.

Examples of this class are: sodium carbonate, sodium phosphate, borax, cane sugar, ferrous sulphate, etc.

5. *Triclinic, Asymmetric, or Clinorhomboidal System*.—Three axes of different lengths, all forming oblique angles with one another. The *doubly oblique octahedron* and the *doubly*

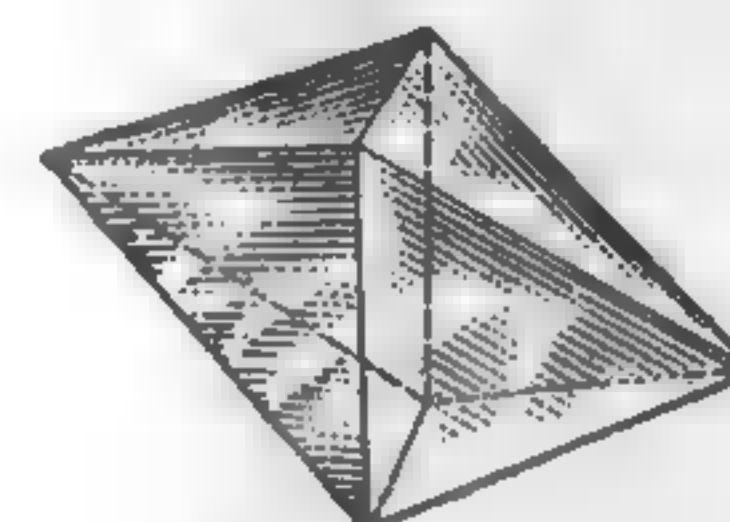


FIG. 12

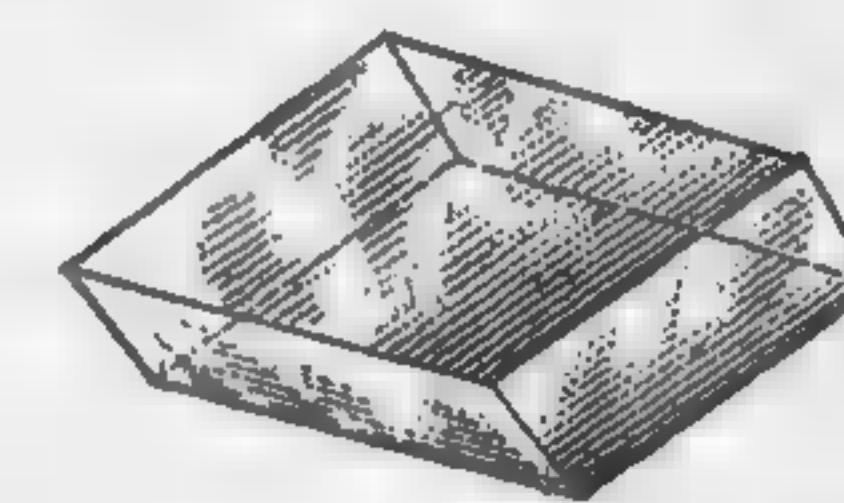


FIG. 13

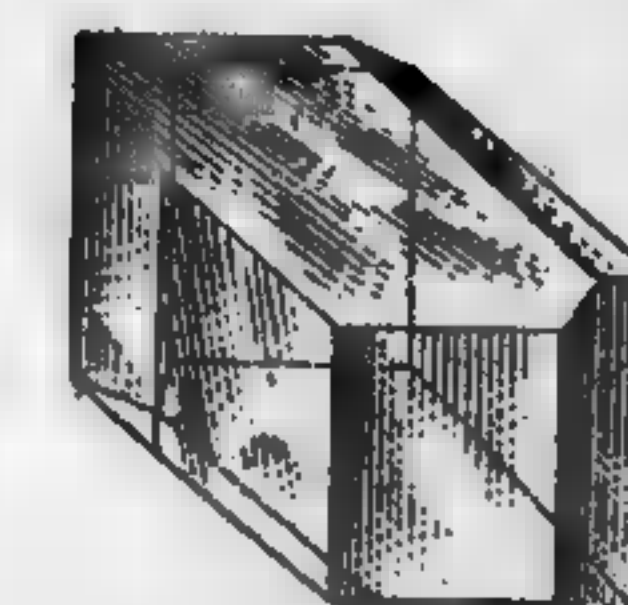


FIG. 14

oblique prism, Fig. 13, are the leading forms of this system. Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, boric acid, the mineral albite, potassium bichromate, and a few other substances are found to crystallize in this system, the forms of which are generally very complicated. The crystalline form of copper sulphate is shown in Fig. 14.

6. *Hexagonal System*.—Four axes, three of these of equal length and cutting one another at angles of 60° , and a fourth

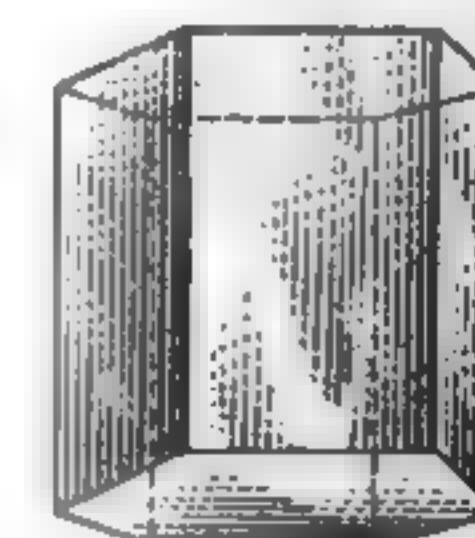


FIG. 15

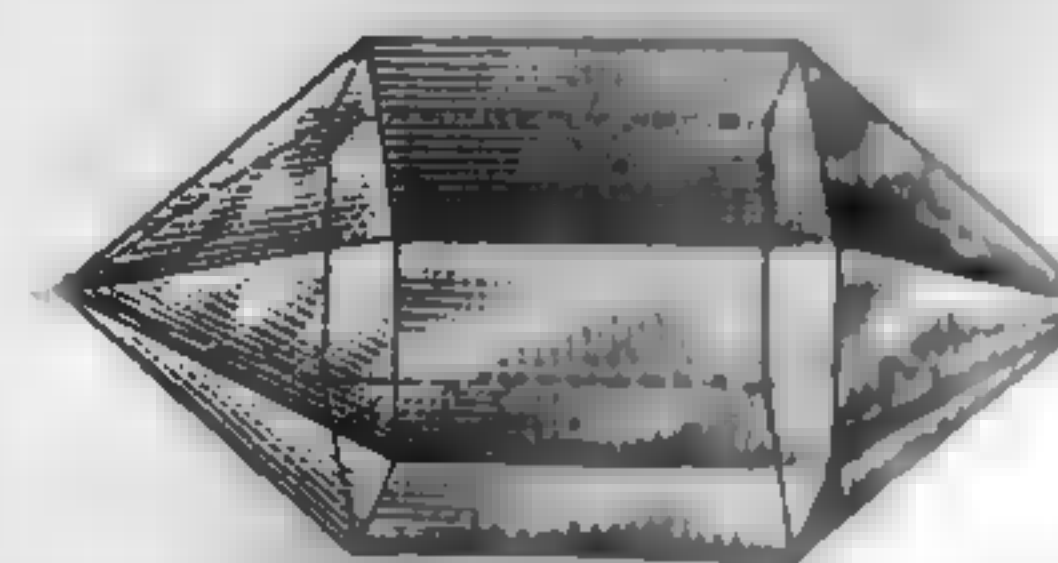


FIG. 16

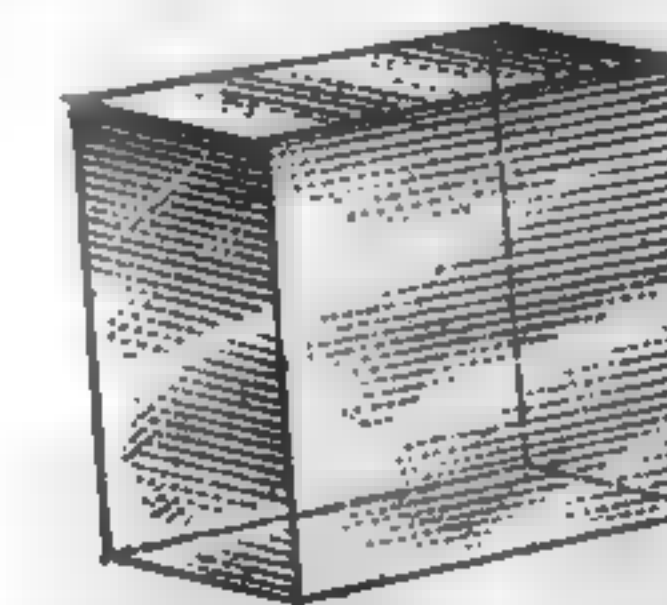


FIG. 17

axis longer or shorter, and perpendicular to the plane of the other three. The *hexagonal prism*, Fig. 15, the *regular six-*

sided pyramid, Fig. 16, and the rhombohedron, Fig. 17, are the common forms of the system.

Examples of this class are: graphite, mercuric sulphide, sodium nitrate, silicic oxide, calcium carbonate, ferrous carbonate, zinc carbonate, etc.

PERIODIC SYSTEM

39. Groups of Elements.—It has long been known that a simple relation exists between the atomic weights of certain elements that, on account of the similarity of their properties, are usually classed together as a group or family.

Thus, the elements lithium, sodium, and potassium are very similar in their properties, and are usually classed together. Their atomic weights are 6.94, 23.00, and 39.10, respectively. An examination of the subject will show that the atomic weight of sodium is approximately the mean of those of lithium and potassium. Thus,

$$\frac{6.94 + 39.10}{2} = 23.02$$

Similarly, chlorine, bromine, and iodine are very similar elements. Their atomic weights are 35.46, 79.92, and 126.92. In this group the atomic weight of bromine is approximately the mean of those of chlorine and iodine. Thus,

$$\frac{35.46 + 126.92}{2} = 81.19$$

The atomic weights of sulphur, selenium, and tellurium are 32.07, 79.2, and 127.5, respectively, and their resemblance to one another is very close. Taking the mean of the atomic weights of sulphur and tellurium, we have

$$\frac{32.07 + 127.5}{2} = 79.78$$

From these and similar cases it would appear that the atomic weights and properties of the elements are in some way related. In 1863-64 the English chemist, J. A. R. New-

0		1		2		3	
A	B	A	B	A	B	A	B
		H, 1.008					
He, 3.99		Li, 6.94		Be, 9.01			B, 10.81
Ne, 20.2		Na, 23		Mg, 24.32			Al, 27.0
Ar, 39.88		K, 39.1		Ca, 40.07		Sc, 44.1	
			Cu, 63.57		Zn, 65.37		Ga, 69.7
Kr, 82.92		Rb, 85.45		Sr, 87.63		Yt, 89	
			Ag, 107.88		Cd, 112.4		In, 114.8
Xe, 130.2		Cs, 132.81		Ba, 137.37		La, 139	
				Er, 167.7		Yb, 172	
			Au, 197.2		Hg, 200.6		Tl, 204
					Ra, 226.4		

TABLE III
PERIODIC TABLE

Series	Families															
	0		1		2		3		4		5		6		7	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1			H, 1.008													
2	He, 3.99		Li, 6.94		Be, 9.01		B, 11		C, 12		N, 14.01		O, 16		F, 19	
3	Ne, 20.2		Na, 23		Mg, 24.32		Al, 27.1		Si, 28.3		P, 31.04		S, 32.07		Cl, 35.46	
4	A, 39.88		K, 39.1		Ca, 40.07		Sc, 44.1		Ti, 48.1		V, 51		Cr, 52		Mn, 54.93	{ Fe, 55.84 Co, 58.97 Ni, 58.68
5				Cu, 63.57		Zn, 65.37		Ga, 69.9		Ge, 72.5		As, 74.96		Se, 79.2		Br, 79.92
6	Kr, 82.92		Rb, 85.45		Sr, 87.63		Yt, 89		Zr, 90.6		Nb, 93.5		Mo, 96			{ Ru, 101.7 Rh, 102.9 Pd, 106.7
7				Ag, 107.88		Cd, 112.4		In, 114.8		Sn, 119		Sb, 120.2		Te, 127.5		I, 126.92
8	Xe, 130.2		Cs, 132.81		Ba, 137.37		La, 139		Ce, 140.25		Pr, 140.6		Nd, 144.3			
9																
10					Er, 167.7		Yb, 172				Ta, 181.5		W, 184			{ Os, 190.9 Ir, 193.1 Pt, 195.2
11				Au, 197.2		Hg, 200.6		Tl, 204		Pb, 207.1		Bi, 208				
12					Ra, 226.4				Th, 232.4				U, 238.5			

lands, attempted to show that this relation extended to all the elements, by placing the elements in a table in the order of their atomic weights. He placed the seven elements having the lowest atomic weights in order in a horizontal line, then placed the eighth under the first, the ninth under the second, etc. Newland's table was very imperfect, and as it failed to show any relationship in many cases, it did not attract much attention. This paper, however, was the forerunner of some valuable work along this line. The table needed to be greatly modified to be of any value, but when sufficiently modified, it was found to express a great law. In 1869 the Russian chemist, D. Mendeléeff, presented a paper on this subject, and in 1870 the German chemist, Lothar Meyer, presented an independent paper on this subject. These papers treated the subject in such a masterly manner, and showed the relation between atomic weight and properties so plainly, that it was then seen that one of the important fundamental laws of chemistry had been discovered. This is known as the *periodic law*. Mendeléeff and Lothar Meyer have done more work on this subject than any one else, and each has proposed several arrangements of the elements in tables to show the relationship between the elements and between their atomic weights and properties. These tables all amount to practically the same thing, but some of them show the relationship more clearly than others.

40. Table III is a periodic table proposed by Lothar Meyer, slightly modified. This probably shows the relationship as well as any, and is very simple. In this table the elements are placed in horizontal lines in the order of their atomic weights; those occurring in the same horizontal line are said to form a *series*. The elements falling in the same vertical line form a natural *family*. After the first three series, the similarity between an element and the one next below it in the same family is not so great as that between it and the second element below it. Consequently, each family is divided into two groups, known as A and B, and the members of each group are more closely related to each other

than to members of the other group of the same family. At the end of the fourth series, the elements iron, cobalt, and nickel occur. These elements are very similar and evidently do not belong in Families 1, 2, and 3; hence, they are classed together as members of Family 8. Copper comes next, and this has some properties that would tend to class it in Family 1. The next elements fall into their proper places without any trouble until we come to the end of the sixth series. Here we have the three similar elements ruthenium, rhodium, and palladium, just as iron, cobalt, and nickel occurred at the end of the fourth series. These are classed together in Family 8 in the same manner. At the end of the tenth series the related elements osmium, iridium, and platinum occur, and these are also disposed of by placing them in Family 8.

41. It will be noticed that there are a number of spaces in the table that are left blank. This is because no elements are known to fill these spaces. The atomic weights and properties of the elements on each side of the spaces are such as to indicate that they are in the proper places, and there are no elements known whose properties would fit them to fill these spaces. It is not thought that elements to fill these places do not exist, but that they have not yet been discovered. When Mendeléeff first arranged a table, there were still more blank spaces than there are at present. A blank space occurred in Series 4 between calcium and titanium, and two blank spaces between zinc and arsenic in Series 5. Mendeléeff predicted that an element would be discovered to fill the gap in Series 4, and gave it the provisional name of ekaboron, and that elements would be found to fill the two spaces in Series 5. To the first of these he gave the provisional name ekaluminum, and to the second, ekasilicon. He described the properties that these elements should have from their position in the system, as shown in the table. In 1875 Lecoq de Boisbaudran discovered gallium, which proved to have exactly the properties predicted for ekaluminum. In 1879 Nilson discovered scandium, whose properties turned out to be exactly those predicted for ekaboron;

and in 1886 Winkler discovered germanium, whose properties are identical with those that Mendeléeff attributed to ekasilicon; consequently, these spaces are now filled; and the fact that the properties of these elements had been predicted from their place in the periodic system shows that the periodic law is one of the fundamental laws of nature. The **periodic law** is usually stated as follows:

The properties of the elements are periodic functions of their atomic weights.

42. **Classification Adopted.**—As the elements are divided into natural families, it would seem most logical to treat them in order, commencing with Family 1. There are several objections to this course, however, the chief one being the fact that in order to understand the chemistry of the first family, familiarity with some of the later families is essential. Hydrogen and oxygen have already been studied, and consequently oxygen will not need to be treated again in the group to which it belongs. A curious thing about the tables prepared is the fact that in none of them is there any place for hydrogen. This element seems to stand without the periodic system, not related closely to any of the elements, but a type of all. As a knowledge of some of the elements occurring in the latter part of the table is necessary in studying those occurring earlier, some of the latter groups will be treated first, but the periodic system forms the basis for the classification adopted in these Sections.

INORGANIC CHEMISTRY

(PART 4)

FAMILY 7, GROUP B

1. General Remarks.—Group B of Family 7 contains the four closely related elements, chlorine, bromine, iodine, and fluorine, known as the *halogens*. Of these, chlorine, bromine, and iodine are more closely related to one another than they are to fluorine. Chlorine, bromine, and iodine are usually found together in nature, but fluorine seldom accompanies them. When the first three elements are found together in nature, chlorine is usually present in the largest quantity, bromine next, and iodine in the smallest quantity. Of these elements, fluorine and chlorine are gases, bromine a liquid, and iodine a solid, under ordinary conditions. Fluorine does not combine with oxygen, but the other members of this group unite with it in a number of proportions.

These elements form some compounds among themselves; for example, iodine forms the compounds $I\text{Br}$, ICl , ICl_3 , and IF_5 . From this it would appear that iodine acts toward bromine with a valence of 1, toward chlorine with a valence of 1 and 3, and toward fluorine with a valence of 5. Its valence in the compounds $I\text{Br}$ and ICl is not certain, however, for $I\text{Br}$ may be $\text{I}-\text{Br}$, $\text{I}\equiv\text{Br}$, or $\text{I}\equiv\text{Br}$; and ICl may be $\text{I}-\text{Cl}$, $\text{I}\equiv\text{Cl}$, or $\text{I}\equiv\text{Cl}$. In such cases, however, what evidence there is usually points to the simplest formula, so that in cases where the choice lies between several formulas, we are probably justified in assuming that the simplest is correct.

The halogens unite with hydrogen and form the compounds hydrochloric acid, HCl , hydrobromic acid, HBr , hydriodic

acid, *HI*, and hydrofluoric acid, *HF*. The first three are gases, while hydrofluoric acid is a volatile liquid; all have strong acid properties. They combine with metals and form salts known as haloid salts. In combination with each other, and with other non-metallic elements, the valence of these elements varies; but toward the metals they appear to be univalent, except in the case of double salts, the constitution of which can be satisfactorily explained only by assuming that 2 atoms of the same element are in combination with each other, and are united to metals by other bonds.

CHLORINE

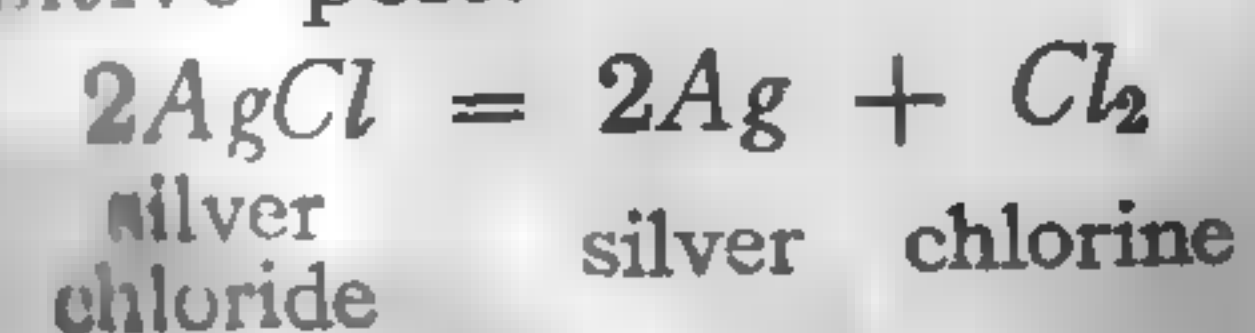
Symbol *Cl*. Atomic weight 35.46. Valence I, III, IV, V, and VII. Density 3.214. Molecular weight Cl_2 70.92. Melting point $-102^\circ C$. Boiling point $-33.6^\circ C$. at ordinary atmospheric pressure. One liter weighs 3.167 grams at $0^\circ C$.

2. History.—Chlorine was discovered by Scheele in 1774, who called it *dephlogisticated muriatic acid*, a name which was afterwards changed by Berthollet to *oxymuriatic acid*. It was first recognized as an element by Gay-Lussac and Thenard in 1809, and by Sir Humphry Davy in 1810, who gave it the name it now bears.

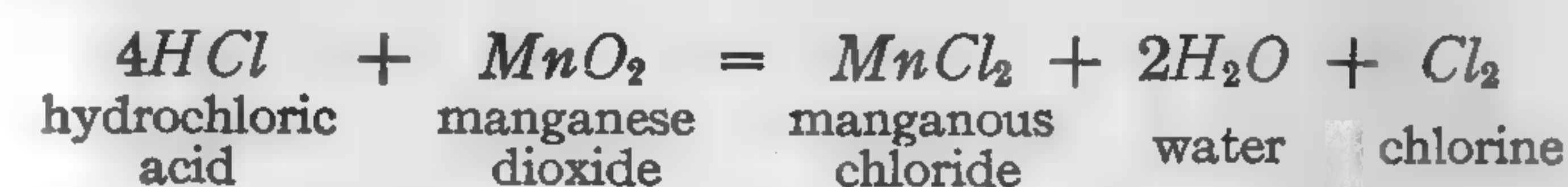
3. Occurrence.—Chlorine is never found in the uncombined state, but is very abundant in the mineral world as sodium chloride, magnesium chloride, potassium chloride, and calcium chloride. Sodium chloride, or salt, exists in sea-water, mineral springs, and in the solid form in the earth, forming vast deposits, many of which are mined.

4. Preparation.—Chlorine may be prepared:

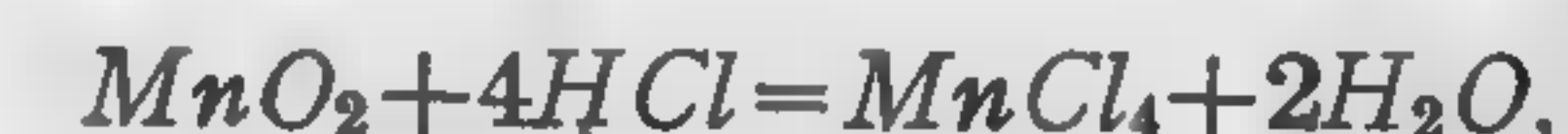
1. By the action of electricity on silver chloride. The pure salt is fused and electrolyzed, carbon electrodes being used. Silver separates at the negative pole and pure chlorine is evolved at the positive pole.



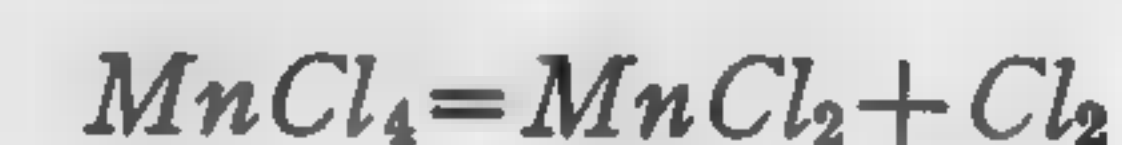
2. By the superior affinity of oxygen for hydrogen, as when, for instance, hydrochloric acid acts on manganese dioxide:



The manganese dioxide first dissolves in the hydrochloric acid and forms a dark-brown solution of manganic chloride:



which on heating decomposes into chlorine and manganous chloride:



Chlorine may be obtained also by the use of potassium permanganate in place of the manganese dioxide:



EXPERIMENT.—The apparatus necessary for the preparation of chlorine is shown in Fig. 1. The materials employed are placed in a flask *A*, which stands in fine, dry sand contained in a shallow iron basin, known as a *sand bath*, on an iron tripod, beneath which a Bunsen burner is placed. Two tubes pass through the stopper of flask *A*, one *B* for the delivery of the gas, the other as a safety tube *C*. This safety tube *C* is a funnel, or thistle, tube bent twice upon itself, as shown in Fig. 1. Its object is to prevent the escape of the evolved chlorine; that is, when any liquid is poured into the funnel, a small portion remains in the bend and acts as a valve, or seal, thus preventing the escape of the gas evolved in the flask. To the delivery tube *B* is attached, by means of a piece of rubber tubing a bottle *D* containing sulphuric acid, to the bottom of which a glass tube passes, and through which the gas is made to bubble, in order to dry it. From this drying bottle it passes through a rubber-tube connection and a long glass tube *E* to the bottom of a collecting jar *F*, where, being heavier than air, it gradually collects. When full, a fact easily ascertained from the green color of the gas, the mouth of the collecting bottle is closed with a glass plate smeared with a little tallow.

For every liter of chlorine gas, 8 grams of manganese dioxide and 50 grams of hydrochloric acid ($5\frac{1}{2}$ cubic centimeters of manganese dioxide and 16 cubic centimeters of hydrochloric acid, according to the measuring glass furnished) are required. The acid is placed in the flask first, the manganese dioxide is then added, and the whole thoroughly shaken up. The evolution of chlorine goes on for a time without heat, but to complete the operation the Bunsen burner beneath must be lighted.

PRECAUTION.—In experimenting with chlorine, great care should be taken to avoid the escape of this gas. Have every possible window open while evolving it, so as to allow as much access of fresh air as possible.

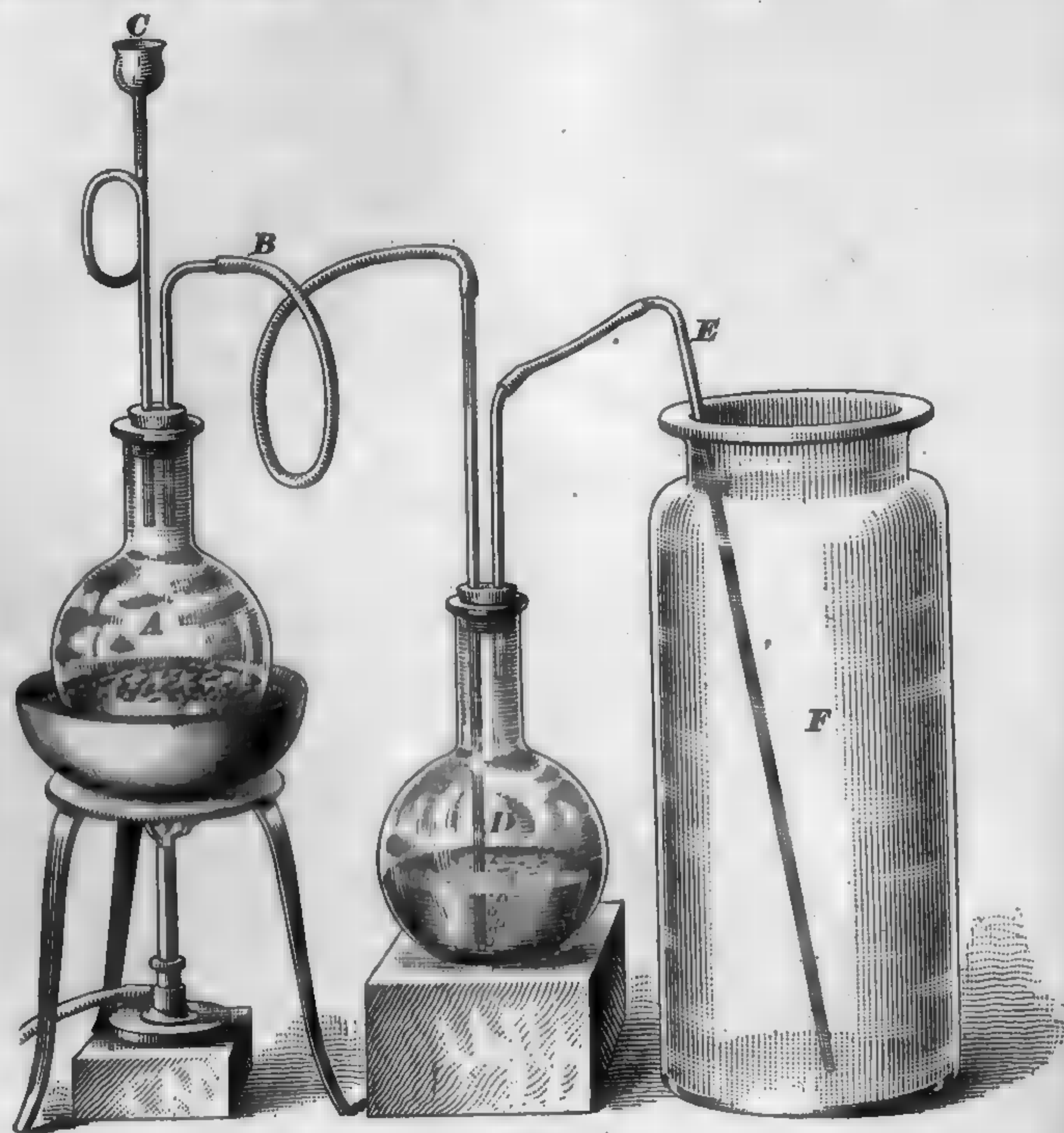
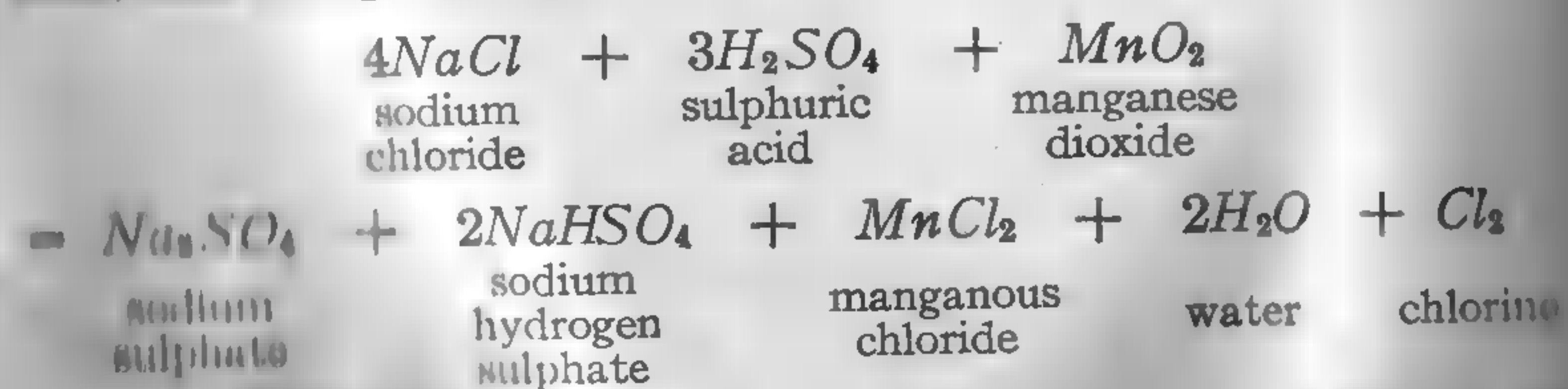


FIG. 1

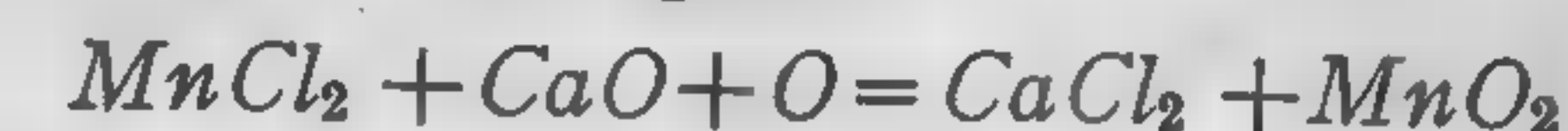
Remember that the inhalation of chlorine will produce a serious inflammation of the respiratory organs.

3. By heating together sodium chloride (salt), sulphuric acid, and manganese dioxide:



The manganous chloride formed is converted by Weldon's regeneration process into manganese dioxide, which can be again

used for the production of chlorine. The manganese dioxide acts as a carrier for the oxygen, which liberates the chlorine. Hence, when the manganous chloride is mixed with lime and air is blown through the mixture, manganese dioxide is again produced, and may be used again.



EXPERIMENT.—Introduce into the retort A, Fig. 2, a mixture composed of 10 grams (6.5 cubic centimeters) of manganese dioxide and 22 grams (19.5 cubic centimeters) of common salt, and to this add 12 cubic centimeters of sulphuric acid diluted with 17.5 cubic centimeters of water.

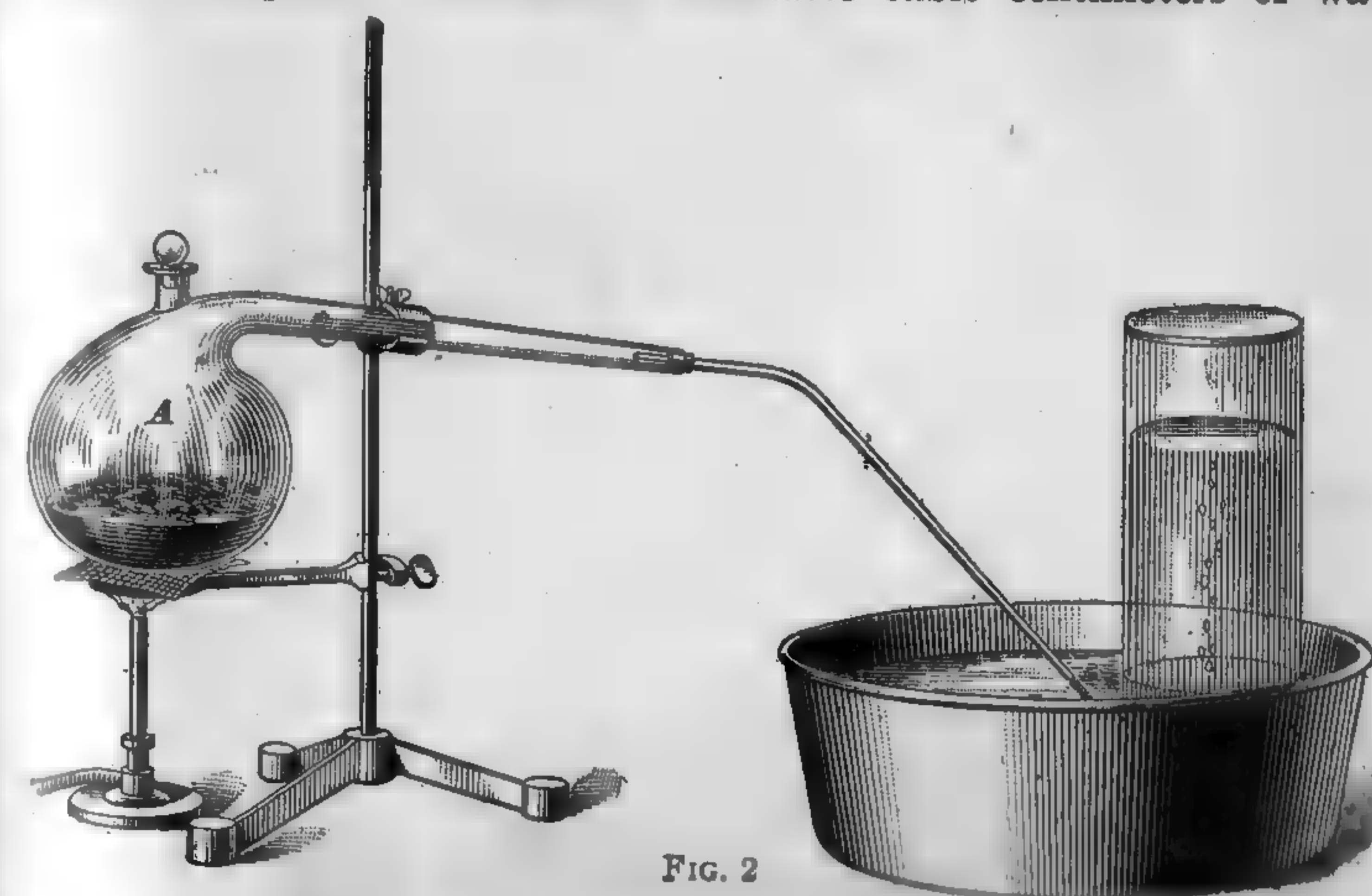


FIG. 2

Shake the retort gently to wet the salt and manganese dioxide, apply a gentle heat to it, and collect the gas in bottles filled with water and inverted in a pneumatic trough. After the bottles have become filled with the chlorine cover the mouths of the bottles, while still under water, with greased glass plates. The first bottle always contains some air from the retort. As the chlorine obtained is moist it should be kept in a dark place to prevent the decomposition of the water.

5. Chlorine is prepared on a large scale for manufacturing purposes, principally by means of the second method. The manganese dioxide and hydrochloric acid are heated in square stone tanks, clamped together by iron rods, and the joints made tight by means of vulcanized rubber. The heat is furnished by a steam pipe. The manganous chloride resulting is converted into manganese dioxide by the Weldon process.

At the present time more than half of the chlorine used is prepared electrolytically. Many patents have been obtained for the manufacture of chlorine by electrolysis, but the one most largely used is the Castner process. In this process a solution of salt brine is placed in shallow vessels of a non-conducting material and made in three compartments. The three compartments communicate with each other by means of a narrow channel underneath the separating partitions. The inner compartment contains water and an iron cathode, and the outer compartments contain the brine and either carbon or platinum anodes. The bottom of the vessel is filled with mercury, and by rocking the vessel the bottom of the outside compartments is alternately covered and uncovered, the bottom of the center compartment being always covered with mercury.

The current passes from the anode to the mercury, evolving chlorine and depositing sodium on the mercury, with which it amalgamates. By the rocking of the vessel the amalgam is carried into the middle compartment where the current frees it from sodium. The sodium acts on the water in this compartment, caustic soda being formed and hydrogen liberated.

6. Properties.—Chlorine is a transparent gas with a yellowish-green color, a peculiar suffocating odor, and an astsingent taste. It produces coughing when inhaled in a dilute state, and serious inflammation of the air passages if inhaled in larger quantities. Its specific gravity at 0°C . is 2.45 (air = 1). It condenses under pressure at ordinary temperature, or under atmospheric pressure at a temperature of -40°C . to a yellow liquid that boils at -33.6°C . and solidifies at -102°C . Liquid chlorine has a specific gravity of 1.469. The critical temperature of chlorine is 146°C ., and its critical pressure is 93.5 atmospheres. The liquid is not miscible with water, has a yellow color, and is a non-conductor of electricity. One volume of cold water dissolves about three volumes of chlorine gas, a liquid that has practically the same proportion as the gas being formed.

7. Chlorine is not inflammable, does not unite directly with oxygen, but does unite very energetically with hydrogen,

hydrochloric acid being formed; the valuable bleaching power of chlorine is due to this property. Chlorine also combines with many metals to form metallic chlorides. In its combinations with other elements a certain amount of heat is evolved and sometimes light is emitted. If a burning jet of hydrogen is plunged into a bottle of chlorine, the hydrogen continues to burn with the production of hydrochloric acid. When a mixture of hydrogen and chlorine is exposed to diffused daylight the hydrogen and chlorine combine slowly; whereas, bright sunlight causes them to unite with explosive violence.

The following experiments will tend to illustrate the readiness with which chlorine unites with other elements:

EXPERIMENT 1.—Drop some finely powdered antimony into a jar of chlorine gas; a shower of brilliant sparkles will be seen and antimony chloride will be formed. A small piece of thin copper foil dropped into a jar of chlorine will immediately take fire.

EXPERIMENT 2.—Melt some metallic sodium in a spoon and immerse in the moist gas; it will take fire at once and burn brightly and white fumes of common salt will be formed.

EXPERIMENT 3.—Cover the letters of some printed matter with ordinary writing ink and immerse in a jar of chlorine gas to which a few drops of water have been added; after a short time the printed letters will gradually begin to appear.

EXPERIMENT 4.—Into a jar of dry chlorine gas place a piece of red cloth. The color will not be affected in any way. Now add a small quantity of water to the gas; the red color will be bleached.

It will be seen from these experiments that chlorine possesses the property of destroying vegetable colors, but that the presence of water is absolutely necessary in order that the operation of bleaching may take place.

EXPERIMENT 5.—Fit up the apparatus used for the generation of hydrogen from zinc and sulphuric acid; attach to it a jet with a piece of rubber tubing, as shown in Fig. 3. Evolve the hydrogen in the manner previously described, and after taking the usual precautions, light the jet and introduce it into a jar of chlorine; notice that the gas continues to burn and that copious fumes are formed. At the same time the yellow tint, characteristic of chlorine, disappears.

The affinity of hydrogen and chlorine for each other is so great that many organic compounds containing hydrogen are entirely decomposed by chlorine.

EXPERIMENT 6.—Take a piece of tow, pull it as loose as possible, saturate with turpentine (a hydrocarbon with the formula $C_{10}H_{18}$), drop it into a jar filled with chlorine gas; it will be found to be decomposed with the evolution of light and heat. The carbon is deposited as soot; the hydrogen again produces fumes of hydrochloric acid.

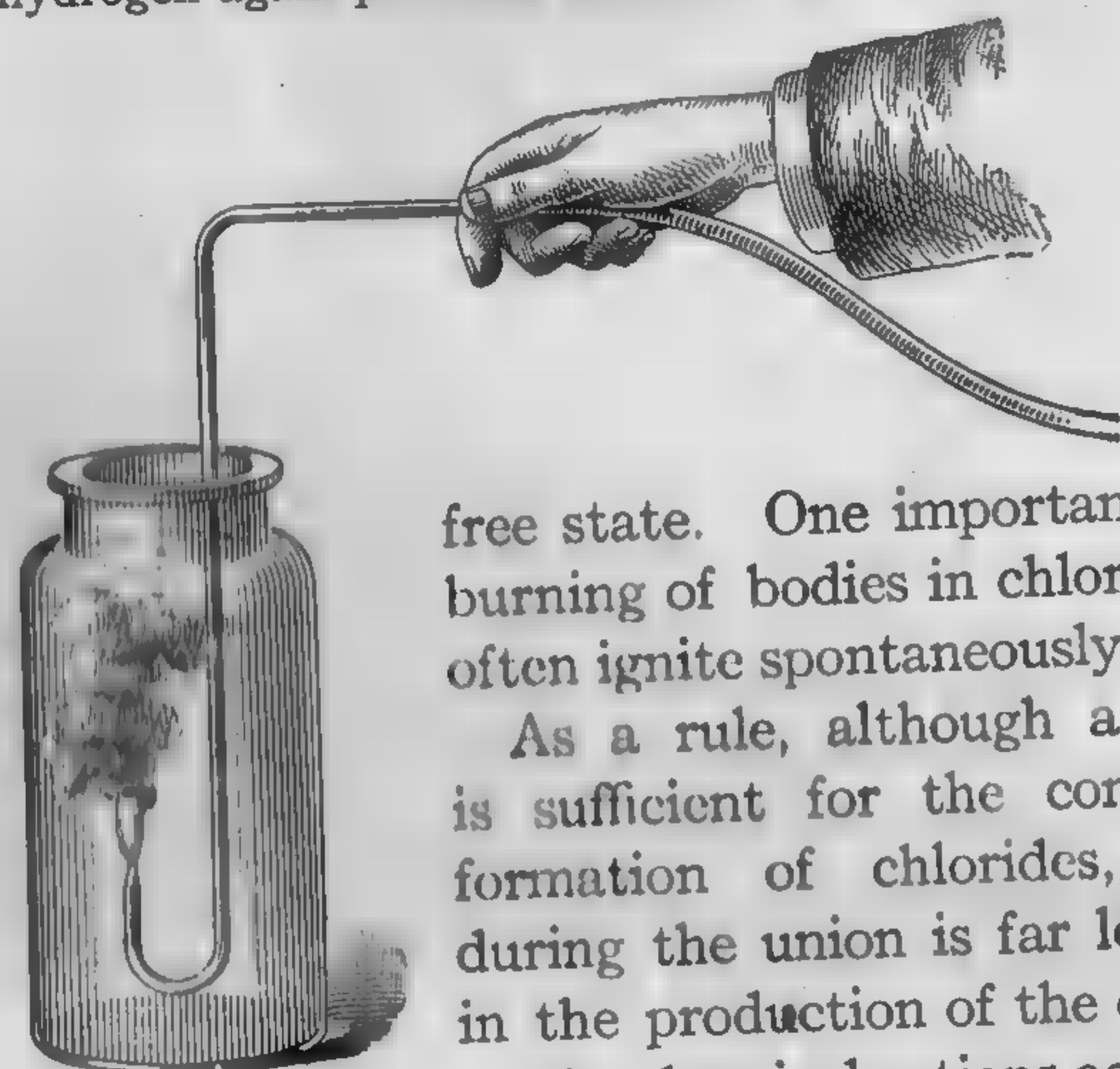


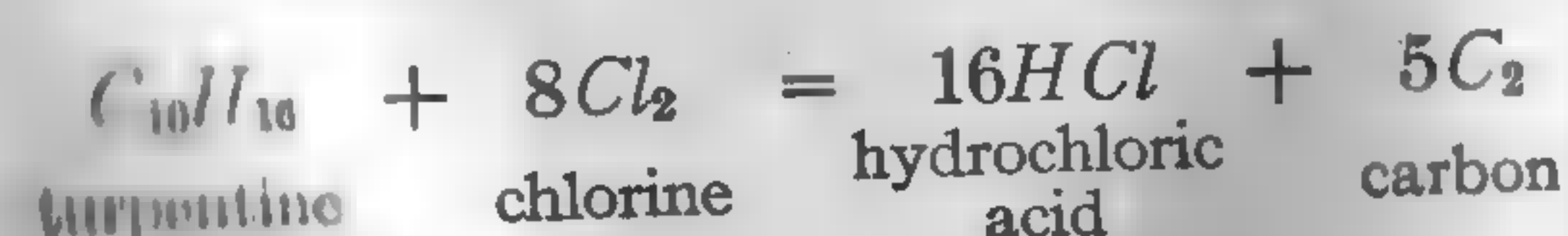
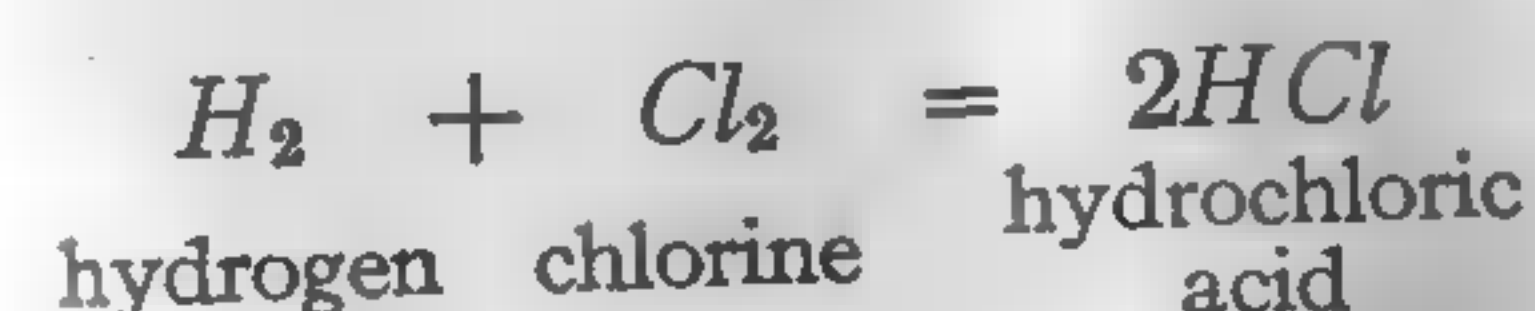
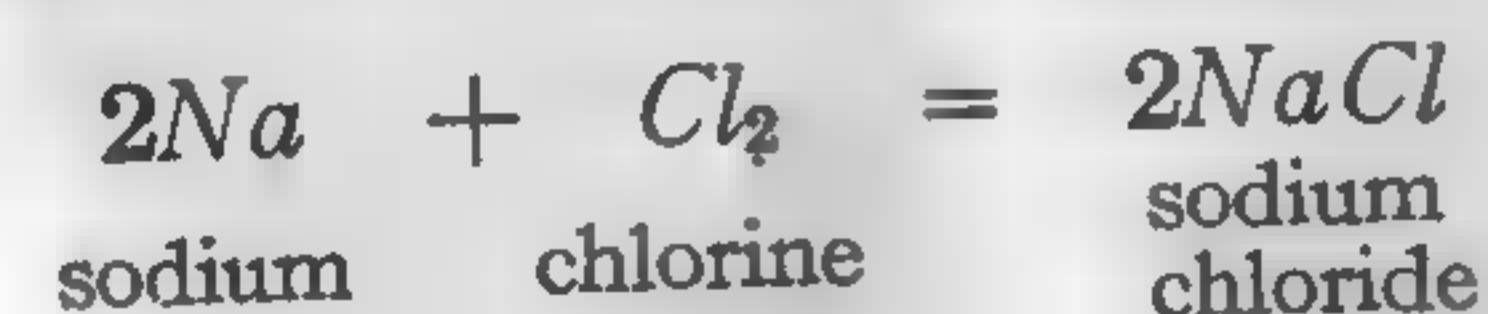
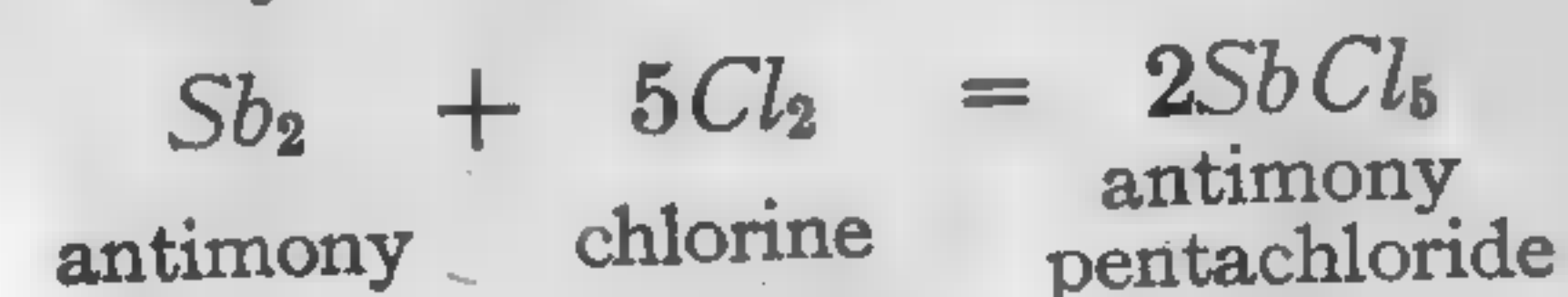
FIG. 3

Carbon does not burn in chlorine, and, if bodies containing it are burned, the carbon is deposited in the

free state. One important peculiarity of the burning of bodies in chlorine is that they very often ignite spontaneously.

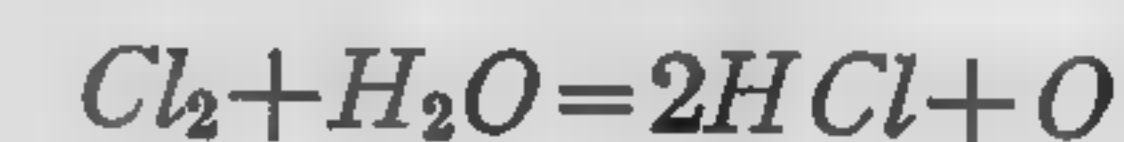
As a rule, although a lower temperature is sufficient for the commencement of the formation of chlorides, the heat evolved during the union is far less than that evolved in the production of the corresponding oxides.

The chemical actions occurring in the experiments in Art. 7 may be represented by the following equations:



8. The bleaching power of chlorine, which has become of great importance in the cotton and paper trades, depends on

the attraction of chlorine for hydrogen. This bleaching action is not possessed by the dry chlorine, but requires water to derive the bleaching effect, as illustrated in Experiment 4. The action depends on the oxidation of the coloring matter, thus destroying the color, by the nascent oxygen of the decomposed water.



Some recent researches tend to show that the bleaching action of chlorine is not due to oxygen alone but is aided by hypochlorous acid formed when chlorine acts on the moisture in the material to be bleached:



Chlorine, as a rule, has no effect on mineral colors, nor will it bleach black tints produced by carbon. (See Experiment 3.) The so-called disinfecting power of chlorine is due to the same property as is its bleaching power. Among the dangerous and offensive products of putrefaction of animal and vegetable matter are hydrogen sulphide, H_2S , ammonia, NH_3 , and similar bodies. These are decomposed by chlorine and the unwholesome properties of the air thus removed; therein lies its value as a disinfectant for badly drained and ventilated buildings, etc. At the present time the greater part of the chlorine manufactured is converted into bleaching powder, or calcium hypochlorite. In this form it can be conveniently transported, and the chlorine may be obtained from it whenever desired. Exposure to the air effects a partial liberation of its chlorine and the addition of hydrochloric or sulphuric acid effects a complete liberation of the chlorine.

9. Summary.—Chlorine is a heavy, yellowish-green gas; does not occur free in nature, but to a very great extent in combination with sodium. It may be obtained from either hydrochloric acid or sodium chloride; it is distinguished by its peculiar, strong odor; it is non-inflammable, but supports combustion; soluble in water, a powerful bleaching and strong disinfecting agent; decomposes water, with evolution of free oxygen.

10. Laboratory Directions.—Chlorine rapidly attacks corks, which may be protected by dipping them into melted paraffin (not paraffin oil, but the solid substance melted in a small dish or basin.)

The fumes produced by burning both phosphorus and antimony in chlorine are poisonous; should the student attempt to perform Experiment 1 or 2, Art. 7, he must be very careful not to inhale these fumes.

The reason why such care must be taken to have dry jars for sodium experiments (see Experiment 3, Art. 7) is that hot sodium accidentally coming in contact with water explodes with great violence; be careful, also, that no water is spilled about the experimenting table.

The student should, if convenient, perform the experiment in Art. 4 and should also prepare a bottle of chlorine water, which may be preserved for analytical work.

Wash all apparatus used for chlorine immediately it is done with; this applies especially to stoppers and rubber tubing.

HYDROCHLORIC ACID

Formula HCl . Molecular weight 36.468. Density 18.23. Melting point $-112.5^{\circ}C$. Boiling point $10^{\circ}C$. under a pressure of 40 atmospheres.

11. History.—Hydrochloric acid, the only compound of chlorine with hydrogen, is sometimes called *muriatic acid*. It was known to the alchemists as *spirit of salts*, but Glauber, in the 17th century, gave it the name of muriatic acid, which is derived from the Latin word *muria*, which means *brine*. The pure hydrochloric-acid gas was first obtained by Priestley in 1772, though it was not until 1810 that its true composition was ascertained by Davy. It occurs in nature in the gases of active volcanoes, in aqueous solutions in the waters of rivers whose source is in volcanic regions, and in the gastric juice of man and of animals.

12. Preparation.—Hydrochloric acid may be formed by the direct union of its elements in the presence of a strong light.

Equal volumes of hydrogen and chlorine may be mixed together and if they are kept in the dark no combination takes place. If the moist gases are exposed to a bright light, or if a flame is brought to the mouth of the jar containing them, or if an electric spark is passed through the mixture, the gases will suddenly combine and produce an explosion. Hydrochloric acid is also formed by the action of chlorine on nearly all hydrogen compounds. Thus, hydrogen sulphide, ammonia, turpentine, water, etc, yield hydrochloric acid when decomposed by chlorine.

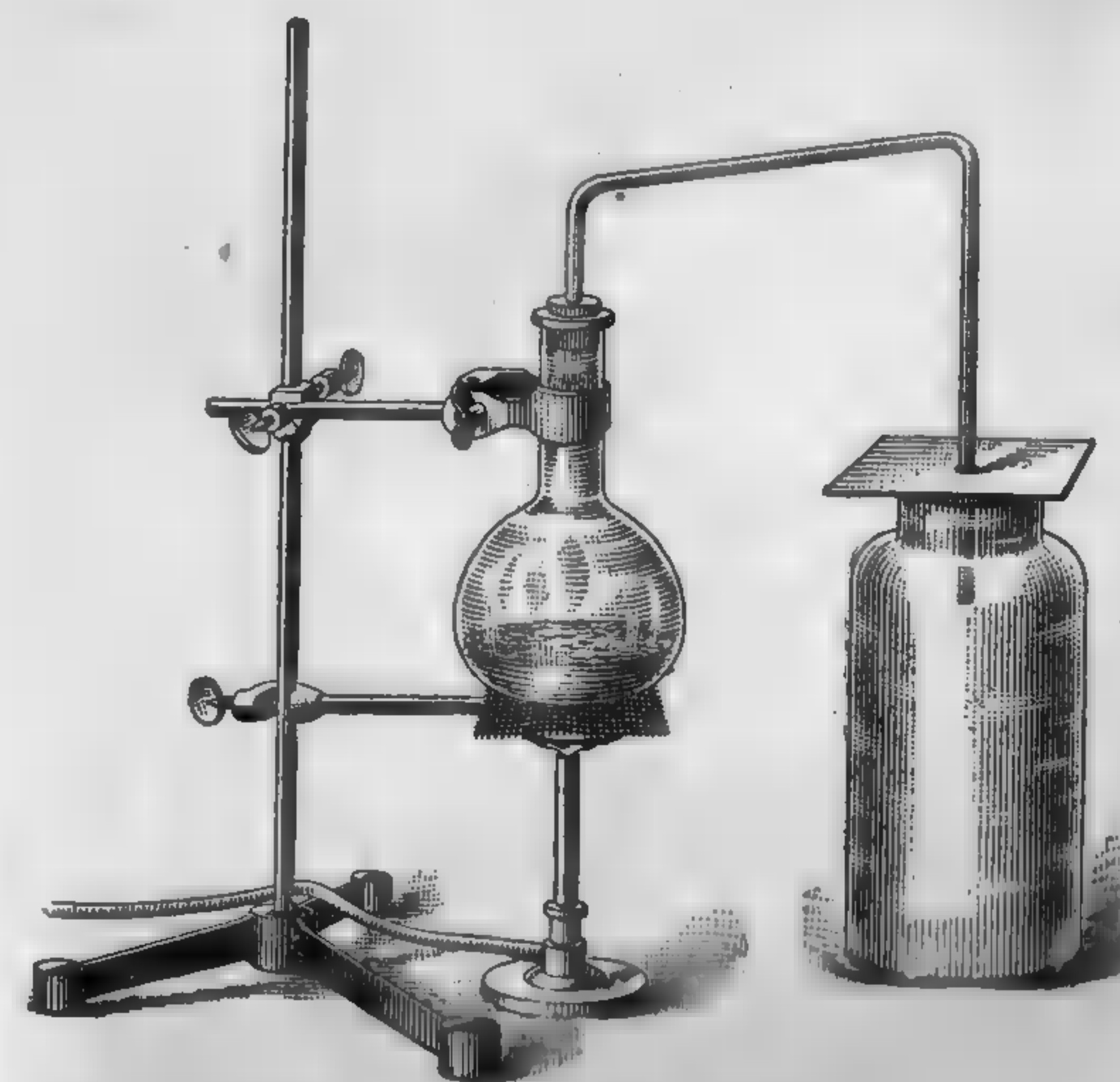
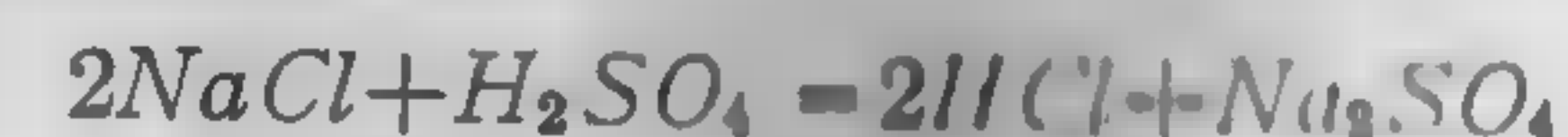
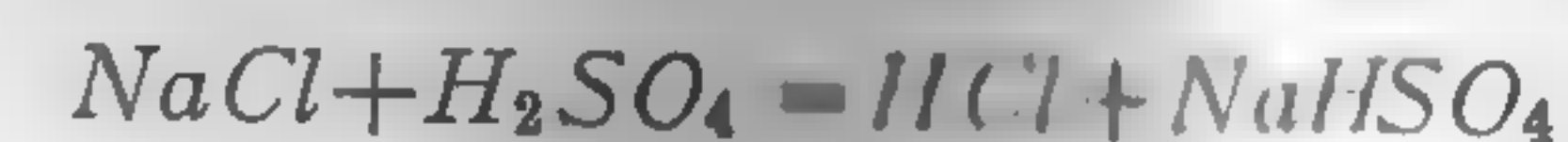


FIG. 4

It is prepared on a large scale by the action of sulphuric acid on sodium chloride, (salt):



If the preparation is carried on at a rather low temperature and an excess of sulphuric acid is used, acid sodium sulphate is formed and a smaller yield of hydrochloric acid is obtained:



EXPERIMENT.—Onto 15 grams (14 cubic centimeters) of common salt contained in a flask (see Fig. 4) pour 25 cubic centimeters of strong sulphuric acid. Close the flask by a perforated stopper containing a tube bent twice at right angles and having one end about four times as long as

the other. The long end passes through a perforated card and nearly to the bottom of a bottle in which the gas is collected by downward displacement. A gentle heat is applied to the flask.

13. Properties.—Hydrochloric acid is a colorless, pungent, acid gas; it fumes strongly in the air, is irrespirable, and extinguishes flame. Subjected to a pressure of 40 atmospheres at 10°C ., or of 2 atmospheres at -70°C ., it is condensed to a colorless, limpid liquid. It is heavier than air, 1 liter weighing 1.6285 grams at 0°C . and 760 mm. pressure. Direct sunlight has no action on a mixture of dry hydrochloric acid and oxygen, but more moisture than is necessary for the complete saturation of the gas causes its gradual decomposition into water and free chlorine. A powerful attraction for water is one of its most remarkable properties.

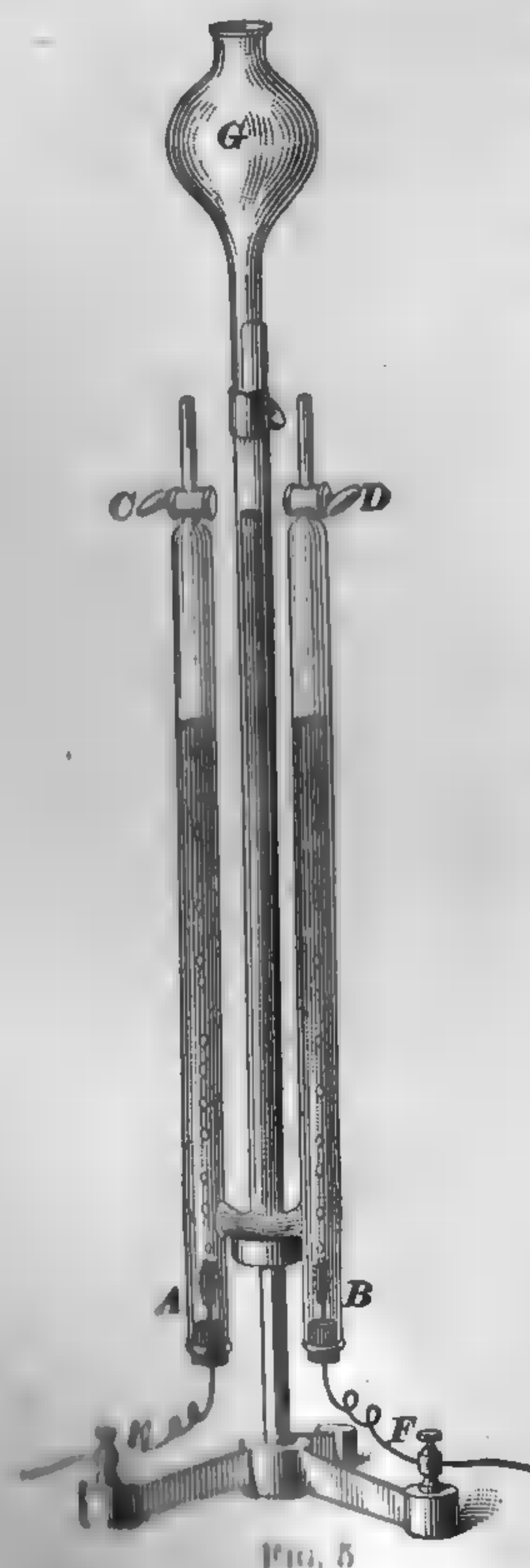


FIG. 5

The muriatic or hydrochloric acid of commerce is simply a solution of the gas in water, and may be recognized by its fumes and the peculiar odor it evolves when exposed to the air. One part of water at a temperature of 0°C . absorbs 503 parts of hydrochloric-acid gas. Hydrochloric acid is employed almost exclusively in the form of this aqueous solution. A solution saturated at 15° contains 42.9 per cent. HCl and has the specific gravity 1.212; the ordinary pure concentrated or fuming hydrochloric acid of commerce usually has a specific gravity of 1.19 and contains 38 per cent. HCl .

14. Composition.—The composition of hydrochloric-acid gas may be determined by plunging a piece of burning metallic sodium into a jar of hydrochloric-acid gas. The combustion

continues, the chlorine uniting with the sodium to form sodium chloride and the hydrogen being liberated. In order to measure the volume of hydrogen, a eudiometer is used. A given volume of hydrochloric-acid gas is placed in the tube over mercury, and sodium or sodium amalgam is then placed in contact with the gas. The gas will be completely decomposed into sodium chloride and hydrogen gas. This will be found to occupy one-half of the original volume. This gas may be ignited, which shows it to be hydrogen. Thus, it is learned that hydrochloric-acid gas is composed of equal volumes of hydrogen and chlorine, and that these elements combine without change of volume to form hydrochloric-acid gas.

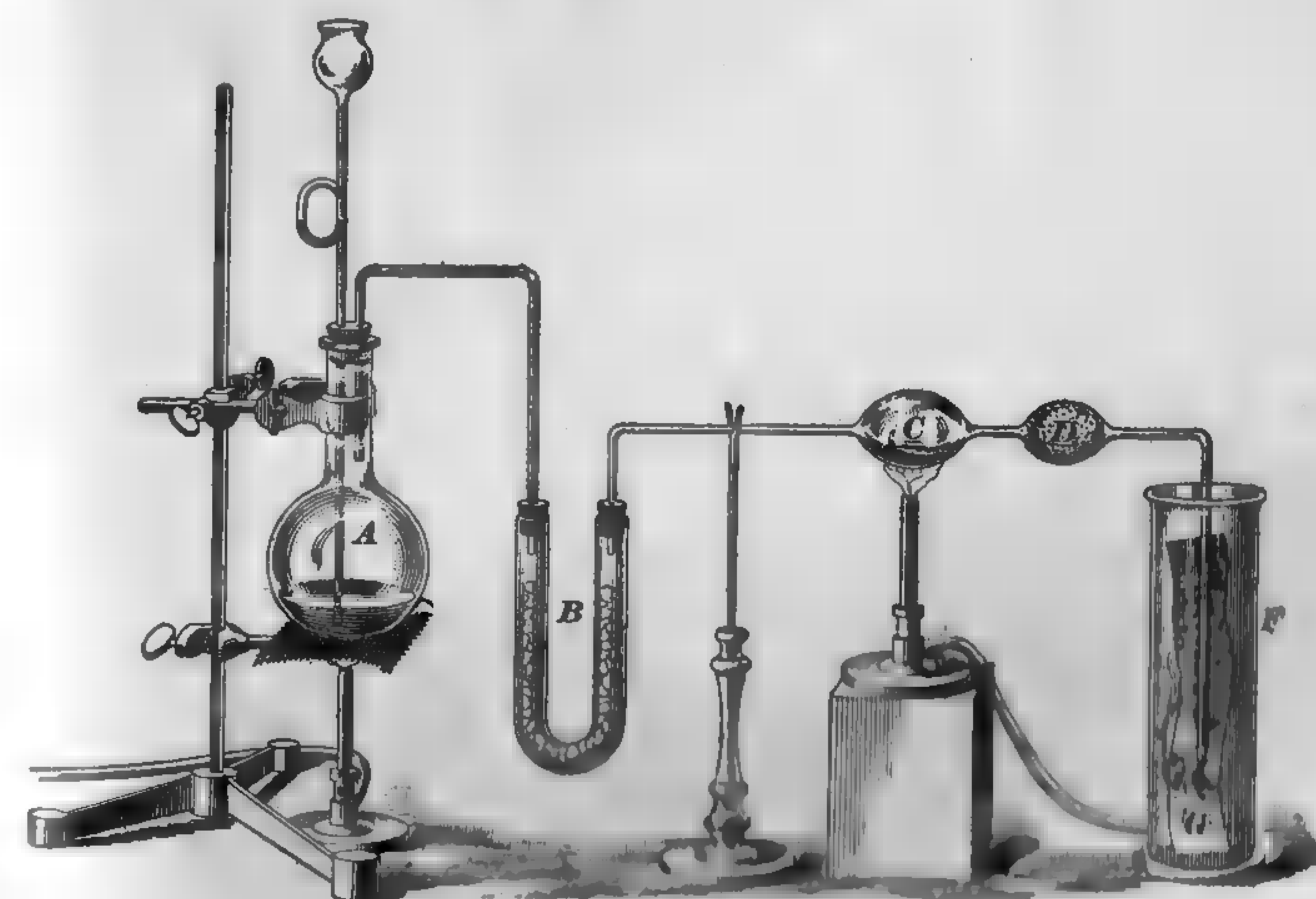


FIG. 6

The composition of hydrochloric acid may also be shown by the electrolysis of the aqueous solution. The apparatus used for this purpose is known as Hofmann's apparatus for the decomposition of hydrochloric acid, and is shown in Fig. 5. It consists of three glass tubes connected at the bottom. The bottoms of the two outer tubes are closed with rubber stoppers through which pass carbon electrodes A and B. Platinum electrodes can be used, but carbon is best, as nascent chlorine acts on platinum. The apparatus is filled to the level of the top-cocks C and D, which are open, through the funnel G. A

battery is connected with *A* and *B* through the wires *E* and *F*. After a time *C* and *D* are closed, when equal volumes of hydrogen and chlorine will collect in the tubes. The hydrogen will rise from the negative electrode and the chlorine from the positive. The chlorine gas can be recognized by its color and the hydrogen by its inflammability. The chlorine can be further recognized by its reddening a piece of blue litmus paper.

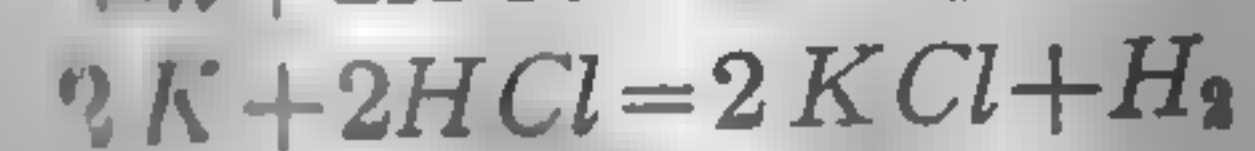
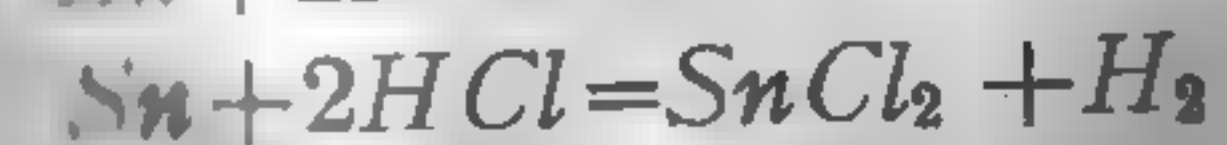
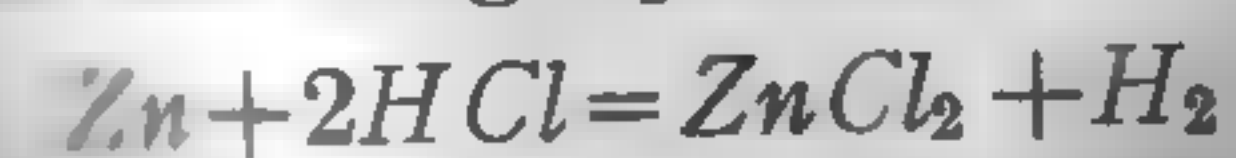
15. Chlorine, like oxygen, is liberated from the electrode connected with the copper or platinum element of the battery. The following eight elements are similar in this respect, and from their behavior with an electric current are called *negative*: Oxygen, chlorine, bromine, iodine, fluorine, sulphur, selenium, and tellurium.

Another convenient apparatus is shown in Fig. 6.

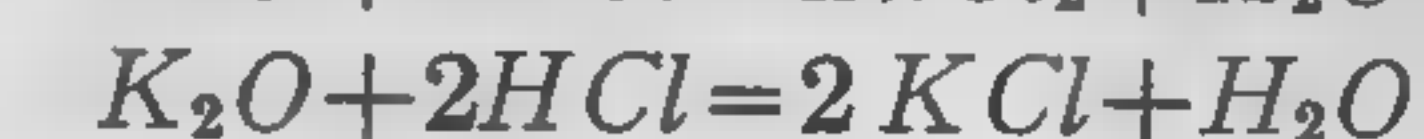
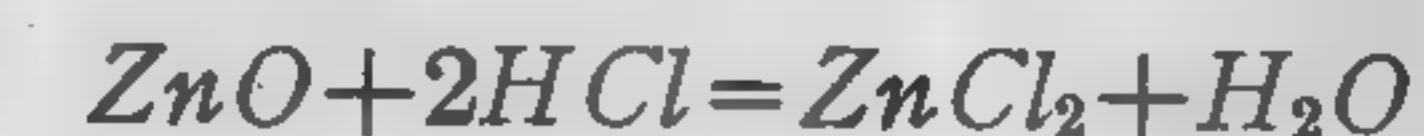
EXPERIMENT.—Fit to the generating flask *A*, Fig. 6, containing salt and sulphuric acid, a U tube *B* containing calcium chloride for the purpose of drying the evolved gas. Connect this to a tube in which two bulbs *C* and *D* have been blown; into bulb *C* introduce some finely powdered manganese dioxide, which should be perfectly dry (this is accomplished by warming it gently in an iron ladle over a Bunsen burner, or placing it on a sheet of tin on a stove for a little while). Arrange a glass jar *F* to receive the escaping gas; place in it a sheet *G* of moist, blue litmus paper. The hydrochloric acid evolved at once changes the color of the litmus paper. Apply heat to the bulb containing manganese dioxide; the hydrochloric acid is decomposed; water collects in the second bulb *D*, and chlorine passes over into the jar *F*. It may be easily recognized by its odor and bleaching power.

16. Uses.—Hydrochloric acid is manufactured on an immense scale as a secondary product in the soda industry, and is used for various purposes in the chemical arts.

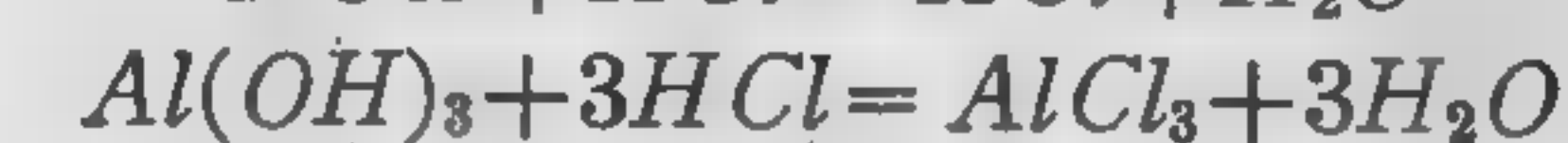
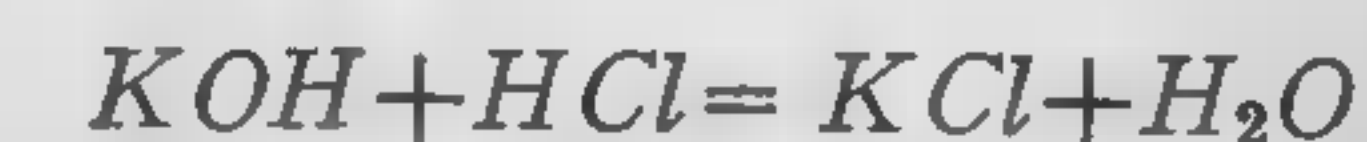
17. Chemical Action.—Some elements like sulphur, nitrogen, phosphorus, boron, and carbon do not act on hydrochloric acid. On the other hand, many elements act on hydrochloric acid, chlorides being formed and hydrogen liberated. This is shown in the following equations:



Again, when hydrochloric acid acts on the oxides of those elements which have the power of setting free hydrogen from it, chlorides are again formed, but instead of hydrogen being liberated water is formed, thus:



This is also true of the action of hydrochloric acid and the hydroxides.



18. Summary.—As the valence of hydrogen is 1, hydrochloric acid is the only existing compound of hydrogen and chlorine. It is easily prepared by the action of sulphuric acid on a chloride. Hydrochloric-acid gas is extremely soluble in water; is colorless and fumes on exposure to air. It has a sharp, pungent odor and sour taste; it is neither inflammable nor a supporter of combustion; it reddens litmus paper; it is composed of equal volumes of hydrogen and chlorine, as has been proved by analysis.

19. Laboratory Directions.—The student should, if convenient, perform the experiment in Art. 12; it is not absolutely necessary in the experiment in Art. 15 that the tube containing manganese dioxide should have bulbs blown in it; a glass tube bent in the shape of a *w* will answer the purpose just as well.

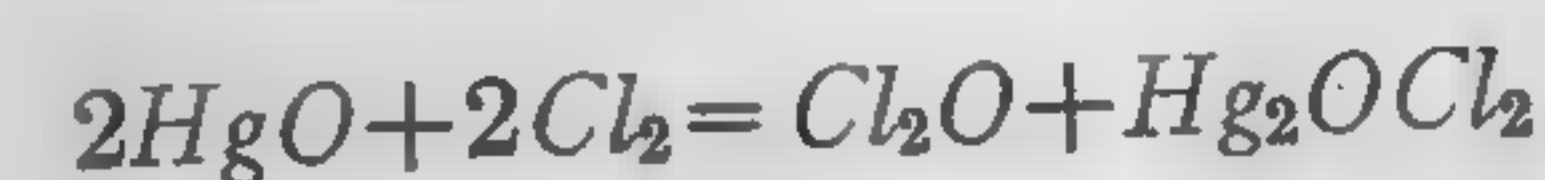
OXIDES AND ACIDS OF CHLORINE

20. Although chlorine combines directly with hydrogen and hydrogen with oxygen, chlorine can not be made to combine directly with oxygen. The compounds formed by the union of chlorine and hydrogen and hydrogen and oxygen are very stable. The compounds of chlorine and oxygen can be formed only by indirect means and undergo decomposition very readily and yield the chlorine and oxygen contained in them. Both chlorine and oxygen are highly electronegative, hence their mutual attraction is limited.

The oxides and acids of chlorine are:

OXIDES	ACIDS
Chlorine monoxide, Cl_2O	Hypochlorous, $HClO$
Chlorine dioxide, ClO_2	Chlorous, $HClO_2$
	Chloric, $HClO_3$
	Perchloric, $HClO_4$

21. Chlorine monoxide, Cl_2O , discovered by Balard in 1834, is formed by passing dry chlorine gas over mercuric oxide:



The gas obtained is condensed in a bent glass tube by means of ice, a stream of cold water, or a freezing mixture of ice and calcium chloride.

It is a reddish-brown liquid which boils at $5^\circ C$. In the gaseous condition it has a brownish-yellow color, a peculiar penetrating odor somewhat resembling that of chlorine, and attacks the respiratory organs very energetically. Its vapor density corresponds to the formula Cl_2O . It is very unstable, decomposing with explosion if heated even by the hands, or when exposed to the action of the electric spark, into two volumes of chlorine and one volume of oxygen.

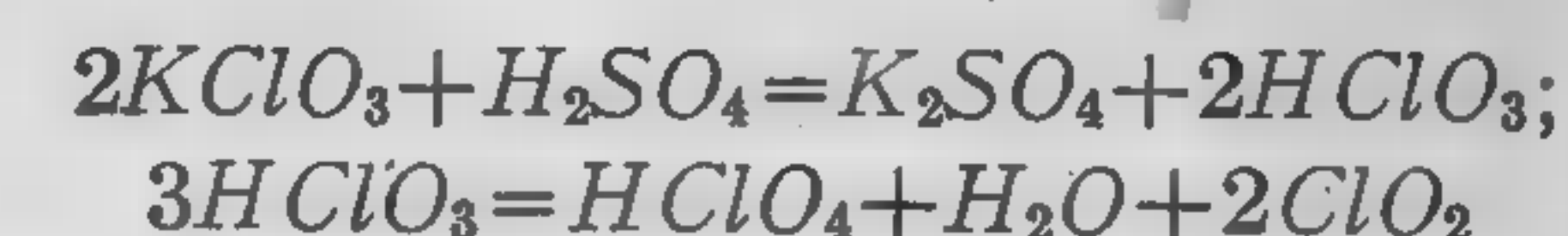


It is also decomposed with violence when brought into contact with sulphur, phosphorus, or an organic substance such as rubber. It has strong bleaching properties. Hydrochloric acid decomposes it into water and free chlorine. It is quite soluble in water, the latter dissolving 200 volumes of the gas at $0^\circ C$., forming hypochlorous acid:



22. Chlorine dioxide, ClO_2 , is an extremely unstable greenish-yellow gas, which can be condensed to a dark-red liquid that boils at $9^\circ C$. and freezes at $-79^\circ C$. to an orange-colored crystalline mass. Its vapor density corresponds to the formula ClO_2 . The gaseous and liquid dioxide are subject to sudden violent decomposition, although the liquid dioxide may be distilled without decomposition if no trace of organic matter

is present. Chlorine dioxide is always formed when sulphuric acid acts on potassium chlorate, and results from the decomposition of chloric acid which is first formed, as shown by the equations:

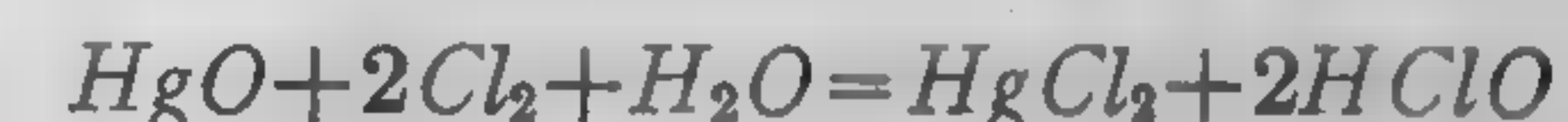


Chlorine dioxide must be collected by displacement, as it is decomposed by mercury and is soluble in water. It possesses a peculiar odor like that of chlorine and burnt sugar.

Combustible substances such as phosphorus, ether, sugar, etc., take fire spontaneously when thrown into chlorine dioxide gas. At $4^\circ C$., water dissolves about twenty times its volume of chlorine dioxide and forms a bright-yellow solution, which is decolorized by alkalis forming salts of chloric and chlorous acids:



23. Hypochlorous acid, $HClO$, is known only in its aqueous solution. It is prepared by passing chlorine monoxide into water, or by passing chlorine into water containing freshly precipitated mercuric oxide in suspension. The liquid must be agitated continually and also kept in the dark.



It has a peculiar odor suggesting chlorine, and is a powerful oxidizing and bleaching agent, owing to the ease with which it decomposes into hydrochloric acid and oxygen. Hydrochloric acid decomposes hypochlorous acid into chlorine and water with the evolution of twice the quantity of chlorine present in the hypochlorous acid:



The hypochlorites are not known in a pure state, but are obtained in solution by neutralizing a solution of the acid by means of bases. They are very unstable.



Boiling a solution of a hypochlorite converts it into a chloride and a chlorate.

24. Chloride of Lime, CaClOCl , or bleaching powder is the most important compound formed by hypochlorous acid. The straight calcium hypochlorite is not known in a pure condition. Chloride of lime is obtained by passing chlorine at ordinary temperatures over slacked lime. The active principle of chloride of lime is the calcium hypochlorite. The reaction governing the preparation of bleaching powder is:



One objection to the view that calcium chloride is present in bleaching powder is the fact that the substance is not deliquescent, as it should be if calcium chloride were present. Again, practically all of the chlorine present in bleaching powder can be expelled by carbon dioxide. This has led to the suggestion that it is a compound of the formula $\text{Ca} \begin{smallmatrix} \text{Cl} \\ \text{OCl} \end{smallmatrix}$

Bleaching powder is a white, porous powder with an odor of chlorine. It has a strong alkaline reaction, and is a strong bleaching agent. It decomposes in the air, and is soluble in water, although the commercial product always leaves a residue of calcium hydroxide.

Dilute hydrochloric or sulphuric acid decomposes it, liberating double the quantity of chlorine found in the contained hypochlorite:

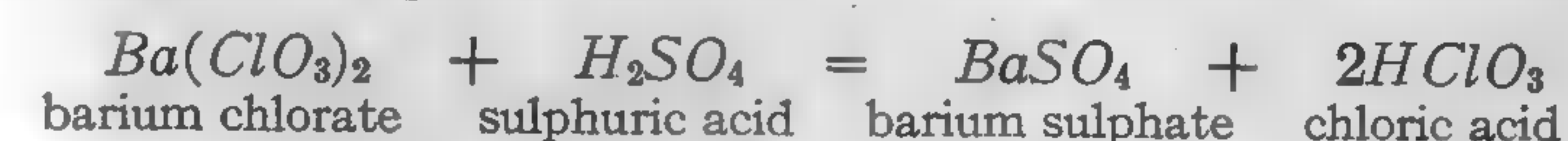


Bleaching powder is used chiefly as a bleaching agent. It does not act very rapidly alone. Carbon dioxide blown through the solution or the addition of dilute acids hastens the action. It is also used as a disinfectant and as an antiseptic.

25. Chlorous Acid.—Although chlorous acid, HClO_2 , has never been obtained, a number of its salts are known, among the most common and important being potassium chlorite, KClO_2 , and silver chlorite, AgClO_2 . Potassium chlorite is obtained by adding a solution of potassium hydroxide to a solution of chlorine dioxide in water; silver chlorite is obtained by adding silver nitrate to a solution of potassium

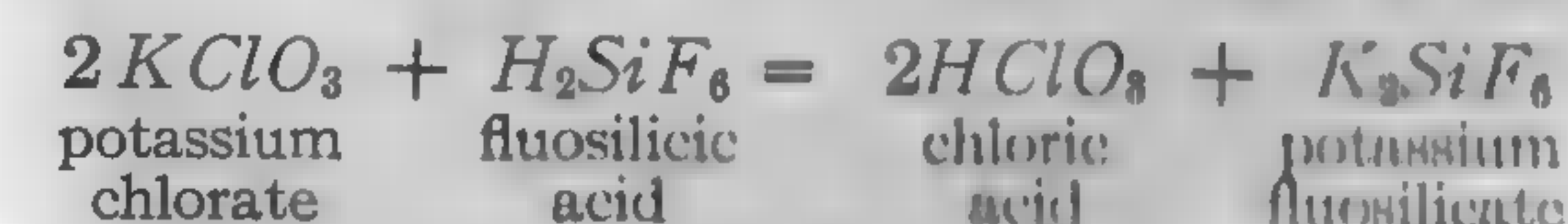
chlorite. The chlorites are all unstable compounds. The alkali chlorites are all soluble in water. If the lead salt is heated for a short time at 100°C . it decomposes with violence, and if rubbed in a mortar with sulphur or with some metallic sulphides it ignites. The soluble chlorites have a caustic taste and bleach vegetable coloring matters. They are distinguished from the hypochlorites by the fact that the addition of arsenious acid does not destroy this bleaching power.

26. Chloric acid, HClO_3 , the most important of the chlorine oxyacids, is prepared by decomposing barium chlorate by means of sulphuric acid:



The clear solution of the chloric acid is poured off from the precipitated barium sulphate, and carefully evaporated in vacuum over strong sulphuric acid. This then contains 40 per cent. of pure chloric acid and corresponds to the formula $\text{HClO}_3 \cdot 7\text{H}_2\text{O}$. Attempts to concentrate chloric acid beyond this point have caused it to break down with a rapid evolution of chlorine and oxygen gas and the formation of perchloric acid.

By adding fluosilicic acid to a solution of potassium chlorate, the latter is decomposed and the potassium precipitated as insoluble fluosilicate, while chloric acid is found in the solution:

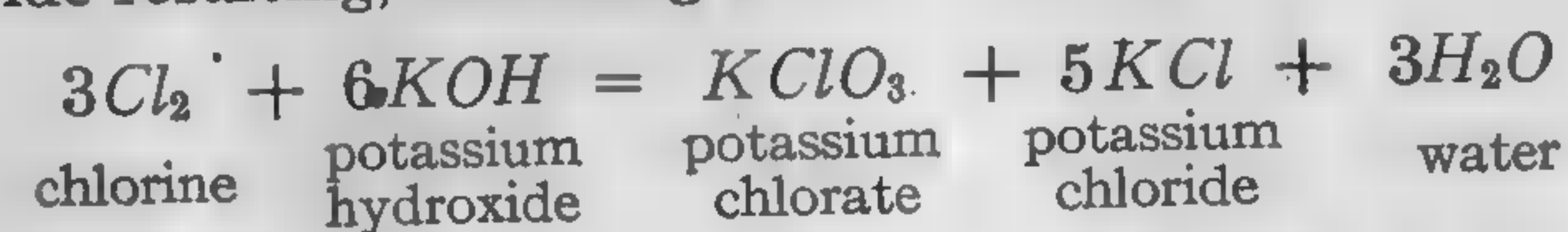


On evaporating the solution at a temperature not exceeding 38°C ., the chloric acid is obtained as a slightly yellow, sirupy liquid with a pungent odor. It has a specific gravity of about 1.28, and contains about 40 per cent. of HClO_3 . It does not change rapidly at ordinary temperatures, but above 40°C . it is decomposed on continued exposure to light according to the equation:



It is a very powerful oxidizing agent. Organic substances such as wood and paper decompose the acid at once, and are themselves oxidized so rapidly as to take fire. An aqueous

solution of chloric acid is colorless, has a pungent smell, a powerful acid reaction, and bleaches vegetable colors quickly. It is a monobasic acid. Its salts, the chlorates, are also very active oxidizing agents. They are used for the preparation of oxygen, and in detonating and pyrotechnical mixtures. It may be obtained by passing chlorine through a hot solution of potassium hydroxide, potassium chlorate and potassium chloride resulting, according to the equation:



All the chlorates are soluble in water, but to a much less extent than the chlorides. Reducing agents (nascent hydrogen, sulphur dioxide) convert them into the corresponding chloride. Chlorates are distinguished from chlorides by the fact that they give no precipitate with silver nitrate. If the chlorate is heated, however, the oxygen is driven off, and the chloride is formed, and this will produce a white precipitate with silver nitrate, in the presence of nitric acid.

27. Perchloric acid, HClO_4 , is formed by the decomposition of chloric acid, but is more conveniently obtained from its salts, the chlorates. When heated to fusion, potassium chlorate at first breaks up according to the equation:



If the heat is removed, no further decomposition takes place, and the perchlorate can be separated from the chloride by treating the mixture with cold water, in which the chloride dissolves readily, while the perchlorate is but slightly soluble. From the perchlorate thus obtained, perchloric acid may be prepared, either by treating it with fluosilicic acid, as in the preparation of chloric acid, or by distilling it with sulphuric acid.

Perchloric acid is the most stable of the oxyacids of chlorine. It is a colorless liquid that fumes strongly in the air. Its specific gravity is about 1.78 at 15° . It may be solidified by lowering the temperature, and when the temperature is raised again melts at about 15° and boils at 110° . It is a dangerous substance to handle, for it produces bad flesh wounds,

and decomposes shortly after being prepared, frequently with a violent explosion. It dissolves in water with a hissing sound, forming the hydrate $\text{HClO}_4 \cdot \text{H}_2\text{O}$, while some facts point to the existence of a second hydrate, $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$.

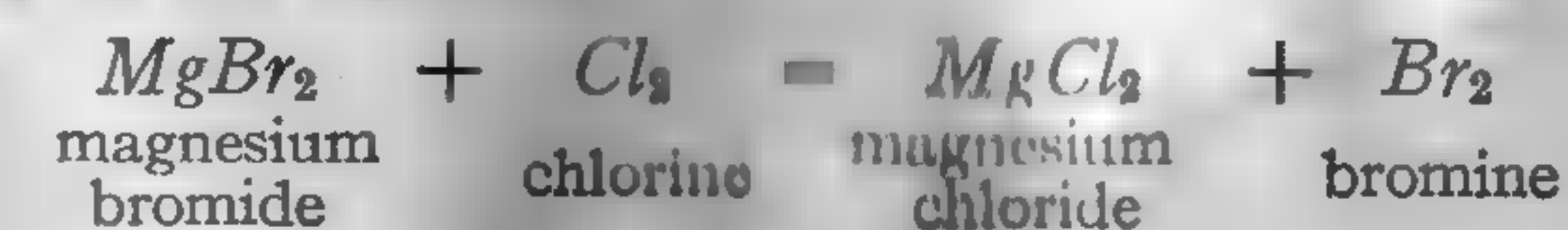
BROMINE

Symbol Br. Atomic weight 79.92. Density 80. Valence I, III, V, and VII. Specific gravity as gas 5.52; as liquid 3.18. Molecular weight 159.84.

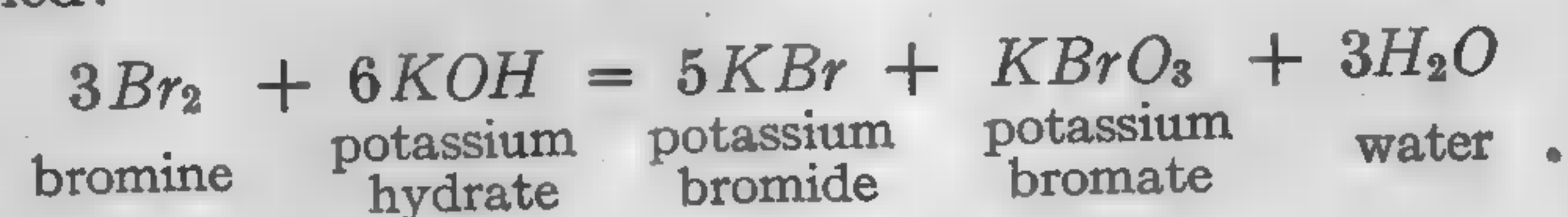
28. History.—Bromine was discovered by Balard in 1826, in the examination of bittern, which is the liquid remaining after the sodium chloride and some other salts have been made to crystallize by evaporating sea-water, which contains only about 1 grain of bromine per gallon in the forms of bromide of magnesium and bromide of sodium. Owing to its disagreeable odor, he gave it the name bromine, which is derived from the Greek word for stench.

29. Occurrence.—Like chlorine, this element is never found uncombined in nature, but always in combination with other elements, such as sodium, potassium, and magnesium. It occurs in the waters of the springs of Kreuznach and Kissingen, in Germany, and during the last few years has been obtained from various saline springs in the United States and from the mother liquors of the salt works at Stassfurt, in Germany.

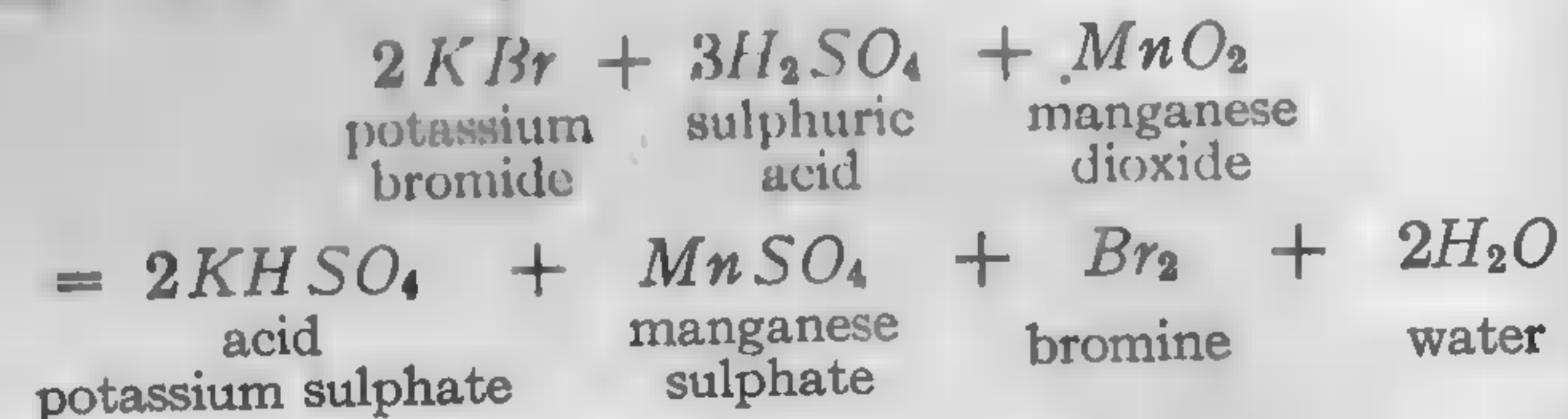
30. Preparation.—The first step in the preparation of bromine is to separate the bromides from the chlorides with which they are associated. The solid salts are dissolved, and then concentrated by evaporation; the chlorides, being less soluble, first crystallize out and leave a mother liquor, or bittern, in which the bromines predominate. There are two reactions by which bromine may be obtained from this liquid. If chlorine is passed through the solution, bromine is liberated according to the equation:



The bromine at first set free imparts a reddish-brown color to the solution. On shaking this with ether the bromine is dissolved, and its ethereal solution rises to the surface, and may be poured from the watery layer underneath. On this ethereal solution being treated with potassium hydrate, its red color disappears, bromide and bromate of potassium being formed:



The ether may be distilled off and recollected; the solid residue of bromide and bromate is ignited in order to decompose the bromate, which splits up into bromide and oxygen in the same manner as does potassium chlorate. In this way potassium bromide is obtained; the bromine may again be liberated by gently heating the bromide with manganese dioxide and sulphuric acid, when an analogous reaction occurs to that which takes place when a chloride is similarly heated:



At times, the mother liquor, instead of being treated with chlorine, is evaporated to dryness and the residue mixed directly with sulphuric acid and manganese dioxide; but, in this case, as chlorides are always present in greater or less quantity, the bromine is liable to be contaminated with chlorine.

31. Properties.—Bromine, at ordinary temperatures, is a dark, brownish-red liquid, so heavy that glass floats readily in it; it possesses an exceedingly penetrating and disagreeable odor, somewhat recalling that of chlorine. At a temperature of 63° C., it boils and is converted into a deep-red vapor that is about five and one-half times denser than air. Bromine freezes at - 7.2° C., forming a dark-brown mass of delicate needles, with a metallic luster. Water dissolves bromine but slightly, 33 parts of it dissolving, at a temperature of 15° C.,

only 1 part of bromine. This solution possesses bleaching powers, but not to such an extent as chlorine. In this, as in other reactions, bromine and chlorine closely resemble each other, but bromine is the less active of the two, and is displaced from its compounds by chlorine. It is an active corrosive poison.

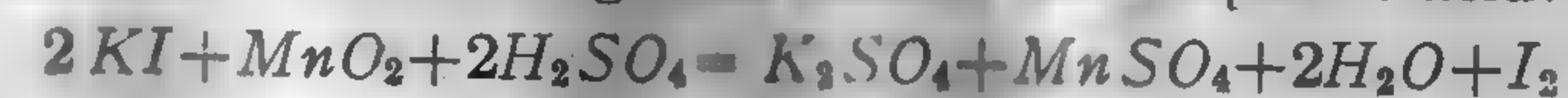
Bromine colors starch yellow, and a bromide in aqueous solution precipitates silver from its solutions as yellow silver bromide. Bromine and its salts are used principally in photography and in medicine.

IODINE

Symbol I. Atomic weight 126.92. Density 126.92. Valence I, III, V, and VII. Specific gravity 4.95. Molecular weight 253.84.

32. History and Occurrence.—Iodine, as well as bromine and chlorine, is found in sea-water, but in considerably smaller quantities. Sodium iodide, *NaI*, appears to constitute a portion of the necessary food of certain varieties of seaweed, which extract it from the sea-water and concentrate it in their tissues. On the coasts of Scotland and Normandy large masses of seaweed were formerly burned in order to extract the soda that they contained. The ash remaining, called *kelp*, or *varec*, was dissolved in water, and the soda salts crystallized out. In the year 1811, Courtois, a soap manufacturer of Paris, being engaged in the manufacture of soda from kelp, obtained from the waste liquors a substance that possessed properties different from those of any matter with which he was acquainted. He turned this substance over to Clement, a French chemist, who satisfied himself that it was an entirely new, and, so far, unknown substance. Davy and Gay-Lussac, in 1813, determined the elementary character of this substance, and named it *iodine*, derived from a Greek word, in allusion to the beautiful violet color of its vapor.

33. Preparation.—Iodine is prepared from its salts in the same manner as is chlorine and bromine, by the treatment of the iodides with manganese dioxide and sulphuric acid:



The mixture thus obtained is heated when the iodine vapor passes over and is condensed.

Iodine is obtained on a large scale from seaweed. On the coasts of Scotland, Ireland, and France the gathering and burning of the seaweed affords occupation for many of the poor inhabitants. The seaweed is spread out to dry, after which it is burned to remove the organic matter. The mineral portions remaining as the ash is known as *kelp*, which contains from .1 to .5 per cent. of iodine. On lixiviating the *kelp*, a concentrated solution of the alkali chlorides, bromides, iodides, carbonates, sulphates, etc. is obtained. The chlorides, sulphates, and carbonates are allowed to crystallize out, sulphuric acid is then added in order to decompose any hyposulphites or sulphides which may be present

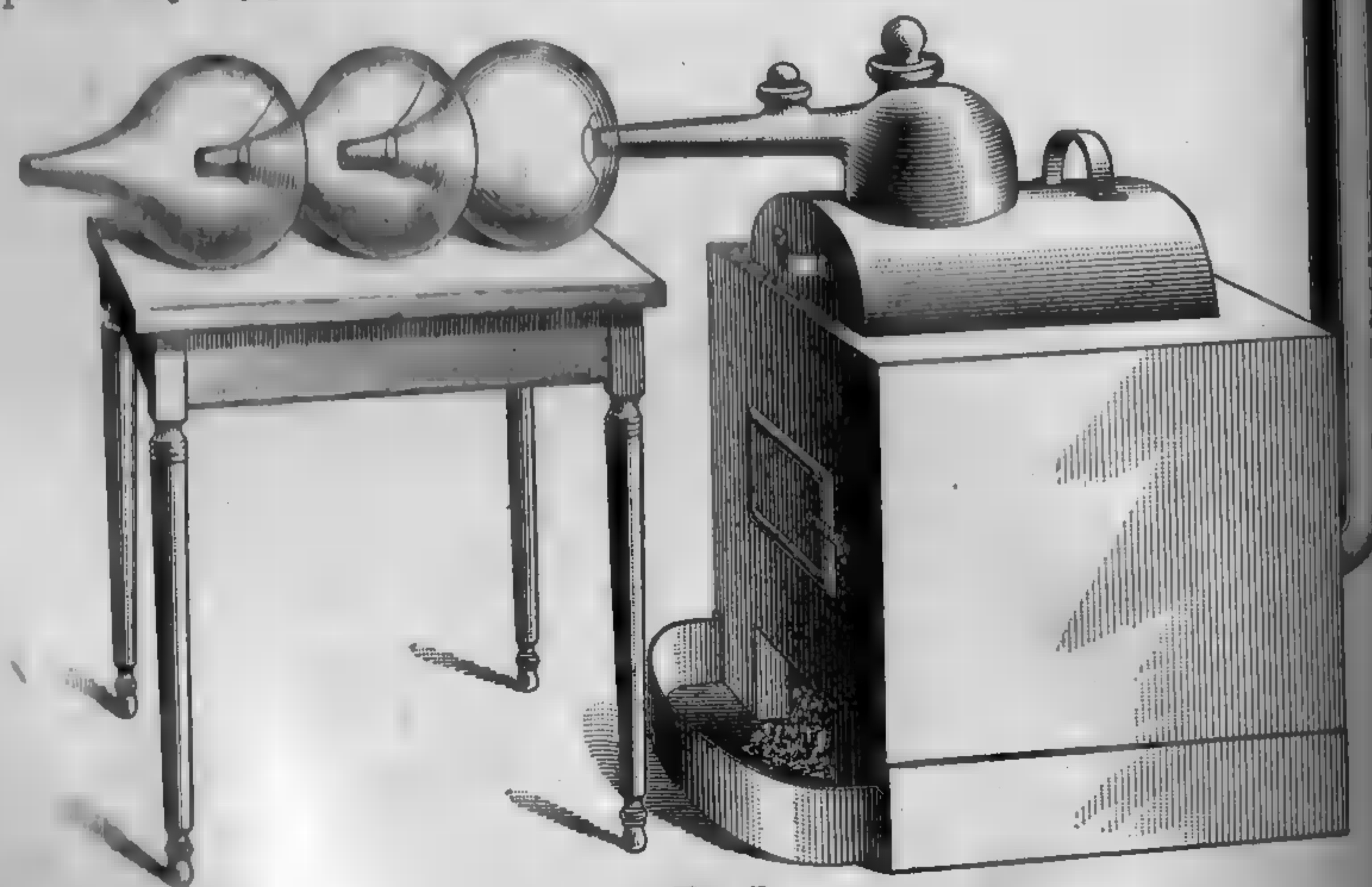


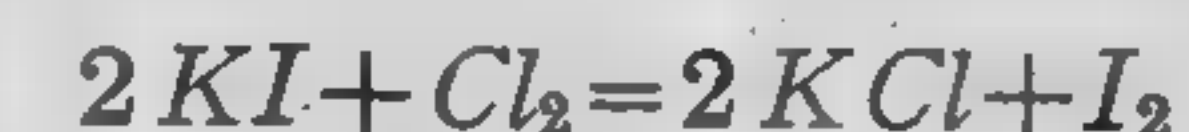
FIG. 7

and which are then allowed to crystallize. The remaining liquor is then treated in several ways to obtain the iodine.

1. The liquors are distilled with a mixture of sulphuric acid and manganese dioxide in iron boilers heated to 60° C. and fitted with lead hoods, Fig. 7. Each boiler is fitted with a lead pipe, which is connected in turn with a series of glass or earthenware condensers, termed *udells*, fitting into each other. The iodine thus obtained is then further purified by

resublimation, but even then it contains traces of the chloride and bromide.

2. In France the iodine is obtained by passing chlorine through the solution containing the iodide when the iodine separates:



If an insufficient quantity of chlorine is used all the iodine is not obtained; whereas, if too much chlorine is used, the chloride of iodine, ICl_3 , is obtained.

3. In later years the largest amount of iodine is obtained from the mother liquors of crude chili saltpeter, $NaNO_3$. These liquors contain the iodine in the form of sodium iodate and iodide. The liquors are treated with sodium bisulphite, the iodine separates out in a solid form, is filtered off, and purified by sublimation. The commercial product thus obtained is washed with a little water, dried on porous plates, and resublimed.

34. Properties.—The features of iodine are well marked; at ordinary temperatures it is a dark-colored (bluish-black) solid, possesses a metallic luster, and gives off small quantities of vapor of a violet tint. It melts at 115° C. and boils at 187° C., evolving a dense, violet, nearly black-appearing vapor that is 8.72 times heavier than air, and is the heaviest vapor known; at 1,700° C., however, the density of this vapor is reduced about one-half. The vapor possesses an odor resembling that of chlorine, which may even be noticed on smelling the substance at ordinary temperatures. Iodine is only very slightly soluble in water, to which it imparts a light yellowish-brown tint, 1 part of iodine requiring about 7,000 parts of water. It dissolves in carbon disulphide and chloroform, to which it imparts a violet tint, resembling the color of its vapor, as well as in alcohol and ether; the two last-named substances form with this element a brown solution. In chemical reaction iodine closely resembles chlorine and bromine, though it is less active than these two elements. It bleaches but faintly, if at all, in full sunlight, but combines directly with all metals to form iodides. Being less active than chlorine and bromine, it

may be liberated from the iodides by the addition of either chlorine or bromine. On the other hand, the oxygen compounds of iodine are far more stable than those of chlorine and bromine.

Starch is the characteristic reagent for free iodine. It strikes with it a deep-blue color, which is so intense that 1 part of iodine may be detected by it in 300,000 parts of water; this blue color vanishes on boiling, but reappears as the liquid cools. Iodine does not give this reaction when in a state of combination. The most delicate test for iodine is the purple-red color it produces when dissolved in carbon disulphide, CS_2 ; 1 part of iodine in 1,000,000 parts of water may be detected in this way. Iodine stains the skin yellow, but is not an active poison.

EXPERIMENT.—Prepare some starch solution by taking a small quantity (about $1\frac{1}{2}$ to 2 cubic centimeters) and shaking it with a test tube full of cold water. Immerse this tube in a beaker of boiling water until the starch gelatinizes, stirring it meanwhile. As soon as the thickening takes place, remove the tube and place it in a beaker filled with cold water, until the starch solution has cooled to a normal temperature.

To a small portion of the starch solution thus obtained add a drop of solution of iodine in water; notice the blue color formed. Heat this blue-colored solution to boiling, and note the disappearance of the blue color, as well as the subsequent reappearance of it, as the liquid cools.

To another portion of starch solution add some potassium iodide; notice that there is no change of color. Add a drop of bromine dissolved in water; a blue color at once forms as a result of free iodine. Repeat the experiment, using chlorine water instead of the aqueous bromine solution, and notice that the same effect is produced.

Add the solutions of bromine and chlorine to separate portions of the starch solution; neither of these produces the blue coloration.

35. Uses.—Iodine, both free and in combination, has found an extended use in the manufacture of aniline colors and in medicine, being particularly serviceable in glandular affections. Its salts are also used extensively in photography.

FLUORINE

Symbol *F*. Atomic weight 19.0. Density 19.0. Valence I and III. Molecular weight 38.0.

36. Occurrence and History.—Fluorine occurs widely distributed in nature, but always in combination with other elements. It is found most frequently crystallized in cubes and octahedra, as the fluoride of calcium, CaF_2 , under the names of *fluorspar*. It also occurs as *cryolite*, a fluoride of aluminum and sodium, $3NaF + AlF_3$. It has also been detected in minute quantities in sea-water and in the water of many mineral springs. Fluorine has also been found in the enamel of the teeth, the bones of mammals, in the blood, the brains, and in milk. It is used in the form of fluorspar (from *fluo*, I flow) as a flux and derives its name from the property this compound has of melting when heated. Owing to its remarkable affinity for other elements, fluorine has resisted until recently all attempts to isolate it.

37. Preparation and Properties.—Hydrofluoric acid is obtained from fluorspar, which is a compound of fluorine with calcium, CaF_2 , by the action of sulphuric acid. After the liquid has been very carefully obtained pure, it is thoroughly dried and strongly chilled. Sodium fluoride is added to make it a conductor of electricity, and it is then subjected to the action of the current in a U tube of platinum, down the limbs of which the electrodes are inserted; the negative electrode is of platinum, while the positive one is made of an alloy of platinum and 10 per cent. of iridium. The U tube is provided with stoppers of fluorspar and platinum delivery tubes for the gases, and is cooled to $-23^\circ C$. The gaseous fluorine evolved at the positive electrode may be freed from hydrofluoric acid, HF , by the passage over dry potassium fluoride, KF . The element is nearly colorless and possesses the properties of chlorine, but much more strongly developed, and has an odor resembling that of hypochlorous acid. It unites directly with hydrogen even without the aid of light, and decomposes water readily. Sulphur, selenium, phosphorus, iodine, arsenic, anti-

mony, silicon, boron, potassium, and sodium take fire in it spontaneously. Potassium chloride and potassium iodide are readily decomposed by fluorine, which liberates the chlorine and iodine. Organic substances are violently attacked and inflamed in it. It liquifies at -187°C. , with the aid of boiling oxygen. In the liquid form it loses, almost completely, its chemical properties. It unites readily, however, with hydrogen, but does not attack glass, iodine, sulphur, or metals.

By igniting platinum fluoride, Moissan has obtained fluorine in an exceptionally pure form.

38. Summary.—The group of elements termed halogens consists of chlorine, bromine, iodine, and fluorine.

Bromine is a dark-red liquid evolving vapor of the same color. It occurs in sea-water, and is obtained from the bromides by the action of sulphuric acid and manganese dioxide. It is similar in general behavior to chlorine, though less active; it may be displaced from its compounds by chlorine.

Iodine is a bluish-black solid with metallic luster that, when warmed, evolves violet-colored vapors. It is found in the ashes of seaweeds, and is obtained by treatment of its salts with sulphuric acid and manganese dioxide. Iodine resembles chlorine to a certain extent, but is less active than bromine. Iodides are decomposed by either free bromine or chlorine. Iodine is characterized by imparting a deep-blue color to starch solution, but only possesses this property when in the free state.

Fluorine is so active that, until recently, it has been practically impossible to obtain it in the free state; it readily attacks glass vessels and decomposes water.

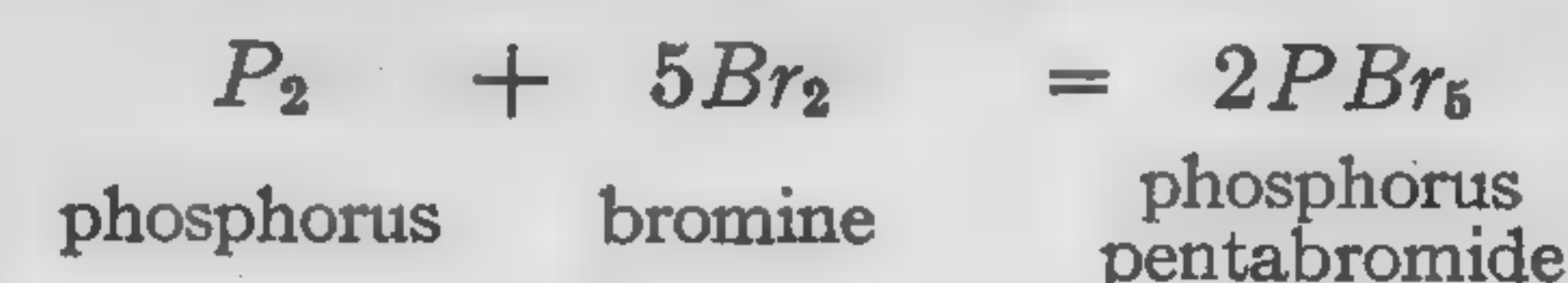
39. Laboratory Directions.—As ether is very inflammable and rapidly evolves a vapor that is highly explosive when mixed with air, great care should be exercised when bringing it near a light. Small quantities only should be used at a time. It should be kept in a so-called store bottle and poured into a $\frac{1}{2}$ -ounce or a 1-ounce bottle, as required, in a room where no lights are burning.

Bromine possesses an overpowering odor; be very careful to get as little of it as possible in your room or laboratory.

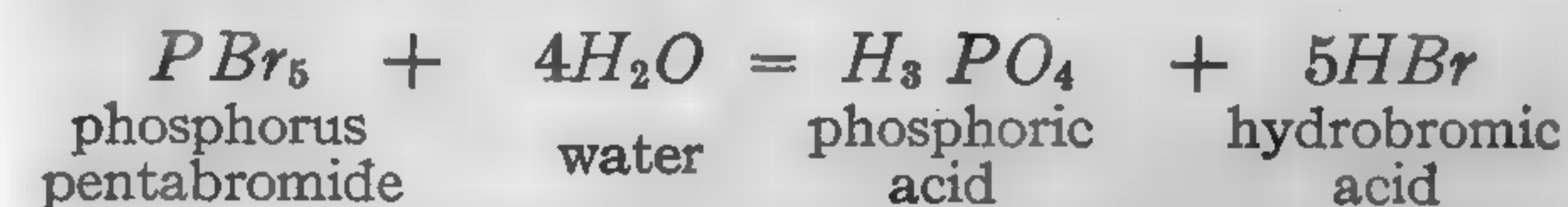
In making a starch solution, take care not to have it too thick; it should be sufficiently thin to pour out like oil.

HYDROGEN COMPOUNDS OF BROMINE, IODINE, AND FLUORINE

40. Hydrobromic acid, HBr , possesses a molecular weight of 80.92 and a density of 40.46. The most instructive method of preparing it consists in attacking phosphorus by bromine in the presence of water, when phosphorus pentabromide is formed according to the equation:



This is decomposed by the water as fast as it is formed, yielding phosphoric and hydrobromic acids:



EXPERIMENT.—To prepare hydrobromic acid, place 5 grams of red phosphorus in the flask *A*, Fig. 8, and pour over it 10 grams of water. Now place about 15 grams of bromine in the funnel *B* and cover with a cover glass. Allow the bromine to drop gradually into the flask *A* by opening the stop-cock *C* slightly. The gas is passed through the *U* tube *D* containing red phosphorus in order to free it of bromine, which might be carried over. The hydrobromic-acid gas is collected by downward displacement in the bottle *E*. A gentle heat may be applied to the flask *A* toward the end of the reaction. This experiment should be performed under a hood or in a well-ventilated room.

Hydrobromic acid can be prepared also by the direct union of hydrogen and bromine vapors. The vapors are passed through a tube containing a platinum spiral heated to redness. As long as the hydrogen is in excess the hydrobromic acid is free from bromine.

It may also be formed by the action of sulphuric acid on a bromide, but, as it is not as stable as hydrochloric acid, it is

partly broken up by the sulphuric acid, and consequently cannot easily be obtained pure in this way.

Hydrobromic acid is very similar to hydrochloric acid; it is a colorless acid gas, fuming strongly in moist air, and is very soluble in water. It liquifies at -73°C ., and the liquid freezes at a temperature of -120°C . It dissolves readily in water, forming a solution having a specific gravity of 1.78 and containing 82 per cent. hydrobromic-acid gas.

41. Hydriodic acid, HI , has a molecular weight of 127.92 and a density of 63.96. It is prepared by acting on

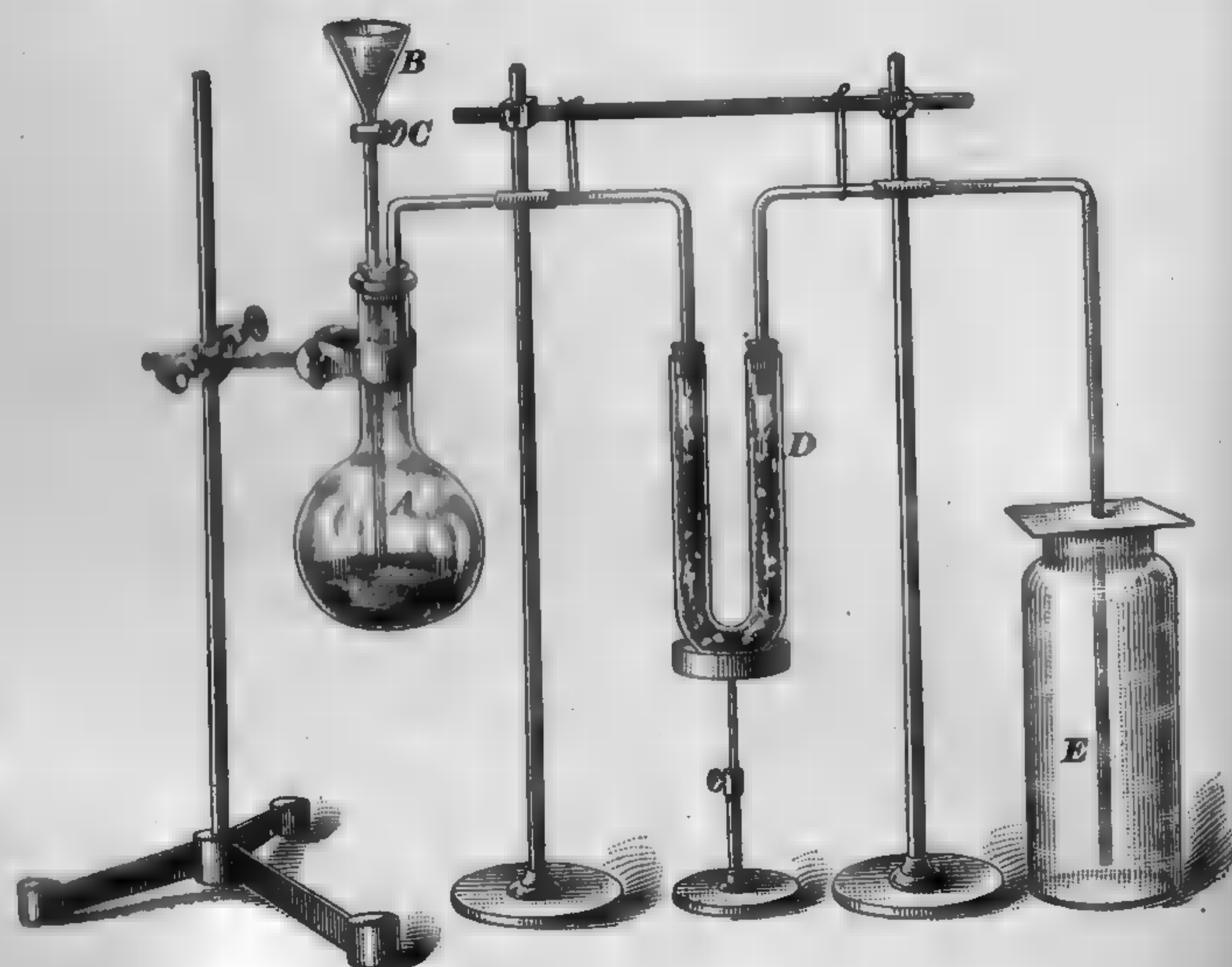
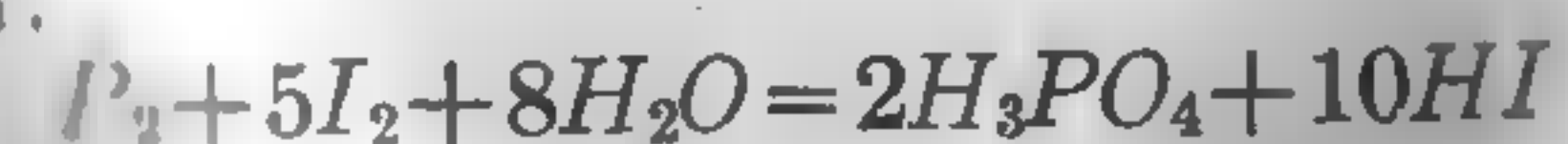
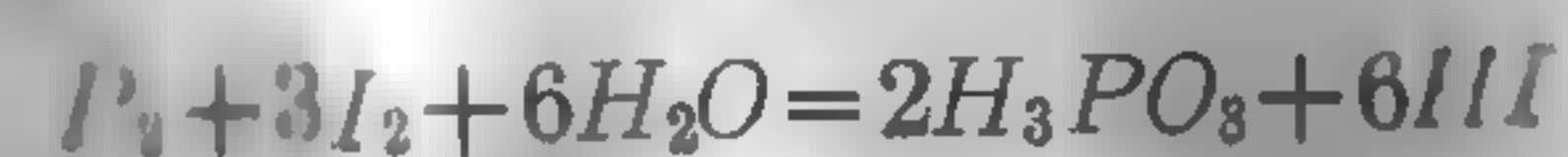


FIG. ■

phosphorus with iodine in the presence of water, when reactions take place that are analogous to those occurring when hydrobromic acid is prepared in the same way and may be expressed in the equation:



Or, if a smaller proportion of iodine is used, the reaction may be:



The hydriodic acid prepared in this way almost always contains some phosphorus compounds.

42. Hydriodic acid, like hydrobromic acid, is a colorless gas, with a specific gravity of 4.41; it has an acid reaction, and fumes in the air. It easily condenses to a liquid by a pressure of 4 atmospheres at 0° ; the liquid thus obtained, when cooled to -55°C ., freezes to a clear, ice-like solid which melts at 51°C . It is soluble in water, like hydrochloric acid, yielding at 0° a solution of specific gravity 1.99. It is less stable than hydrobromic acid, as it gives up its hydrogen more readily; consequently, it cannot be prepared by acting on an iodide with sulphuric acid, for the hydriodic acid is decomposed as fast as formed, depositing free iodine.

If allowed to stand, the solution of hydriodic acid in water soon begins to decompose. The oxygen of the air combines with the hydrogen, forming water and setting free the iodine, which gives the solution a brown color.

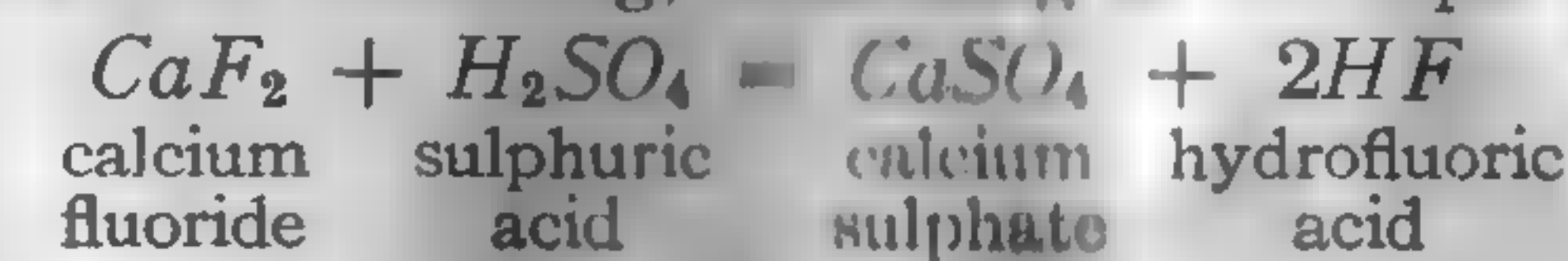
The tendency of the hydrogen of hydriodic acid to combine with oxygen makes this acid a powerful reducing agent. In organic chemistry, hydriodic acid is very frequently employed for introducing hydrogen into a compound; for instance, by heating benzene with hydriodic acid, the benzene may be made to take up 6 atoms of hydrogen:



Since the attraction of iodine for hydrogen is so feeble, metalepsis does not occur between this halogen and hydrocarbons.

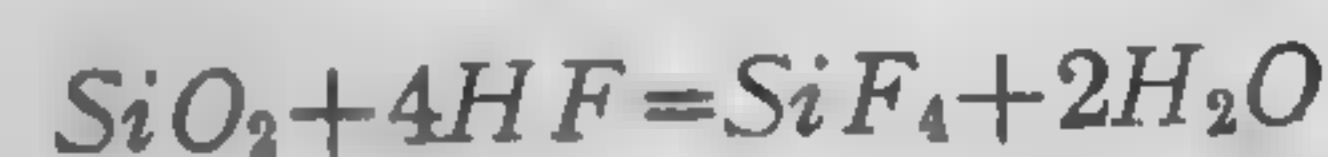
The fact that the organic compounds containing iodine are, as a rule, much less volatile and consequently more manageable than those of chlorine and bromine leads to the extensive use of this element in researches on organic substances.

43. Hydrofluoric acid, HF , has a molecular weight of 20 and a density of 10. It is the most important compound of fluorine, and is prepared either by the action of sulphuric acid on calcium fluoride, calcium sulphate and hydrofluoric acid resulting, according to the equation:



or by heating dry acid potassium fluoride, KHF_2 , to redness in a platinum still. The hydrofluoric acid thus obtained is a colorless liquid that boils at 19.4°C ., and has a specific gravity of .985 at 12° ; it solidifies at -102° and melts at -92° . It has a most pungent, irritating odor, which, when inhaled in even small quantities, causes serious irritation of the lungs. The acid corrodes the skin when brought in contact with it and creates painful ulcers.

Hydrofluoric acid dissolves all metals except lead, gold, and platinum, and has only a slight action on magnesium. It dissolves sodium and potassium as does water. It decomposes the oxides of silicon and boron. When perfectly dry it has no action on glass, but the slightest trace of moisture causes it to decompose glass, the silica contained being dissolved, according to the reaction:



Hydrofluoric acid decomposes metallic silicates, forming a metallic fluoride, which is in turn decomposed by either sulphuric or hydrochloric acid. Its action on glass is well illustrated by the following experiment:

EXPERIMENT.—Coat a glass plate with wax or paraffin and after it has hardened draw or write on it with a needle. Care must be taken to have the needle penetrate the wax to the glass plate. Place some powdered fluorspar in a small lead dish and add some concentrated sulphuric acid to the fluorspar. Place the glass plate, wax side down, over the dish and allow it to remain for about 30 minutes. Remove the glass plate and clean off the wax with the aid of heat. The writing or drawing will be found to have been etched into the glass.

OXIDES AND ACIDS OF BROMINE AND IODINE

44. The compounds of bromine and iodine with oxygen and hydrogen are very similar to the corresponding compounds of chlorine. The compounds formed by bromine are hypobromous acid, HBrO ; bromic acid, HBrO_3 ; and possibly perbromic acid, HBrO_4 . The compounds formed by iodine are iodine pentoxide, I_2O_5 ; iodic acid, HIO_3 ; periodic acid, H_5IO_6 .

45. Hypobromous acid, HBrO , has not been prepared in a pure state because of its instability. Its salts are pre-

pared by a method similar to that used for the preparation of the hypochlorites. Bromine acting on a dilute solution of potassium hydrate produces potassium hypobromite according to the equation:



Bromine vapor acting on calcium hydrate (slaked lime) forms a compound similar to bleaching powder.

46. Bromic acid, HBrO_3 , has not been obtained in a pure state, but its salts are prepared in the same manner as the chlorates. By treating a concentrated solution of potassium hydrate with bromine, potassium bromate is obtained according to the equation:



In chemical behavior the bromates resemble the chlorates.

47. Perbromic Acid.—There is considerable doubt in regard to the existence of perbromic acid, HBrO_4 . One investigator claims to have obtained it as an oily, colorless liquid by decomposing perchloric acid with bromine, but others have failed to get it by this or any other method.

48. Iodine pentoxide, I_2O_5 , is a white solid that is obtained by heating iodic acid to 170°C . It dissolves readily in water, forming iodic acid, and is therefore iodic anhydride, or the anhydride of iodic acid. It is decomposed when heated to 300°C , and is the most stable of any of the compounds of the halogens with oxygen.

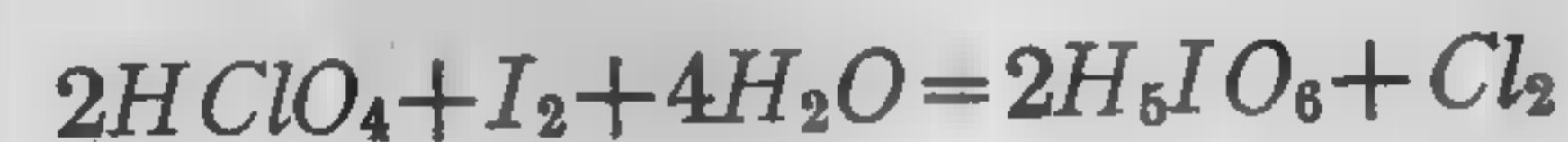
49. Iodic acid, HIO_3 , is similar to chloric and bromic acids, but is more stable. It can be prepared by treating iodine with a strong oxidizing agent, as, for example, concentrated nitric acid. It can also be obtained by passing chlorine through water in which iodine is suspended, when iodic and hydrochloric acids are formed according to the equation:



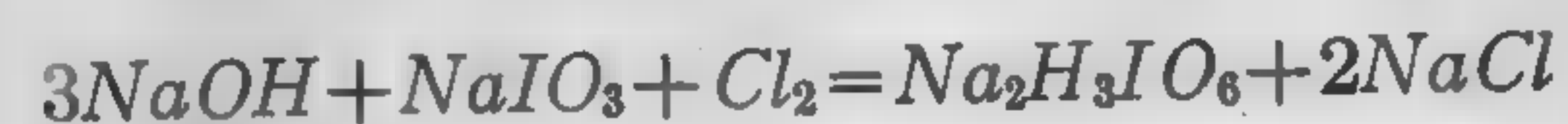
Iodic acid is a crystalline solid that decomposes into water and iodine pentoxide at 170°C ., according to the equation:



50. **Periodic acid, HIO_4 .** The normal acid is not known. The hydrate, $HIO_4 \cdot 2H_2O$, or H_5IO_6 , is formed by the action of iodine on perchloric acid:

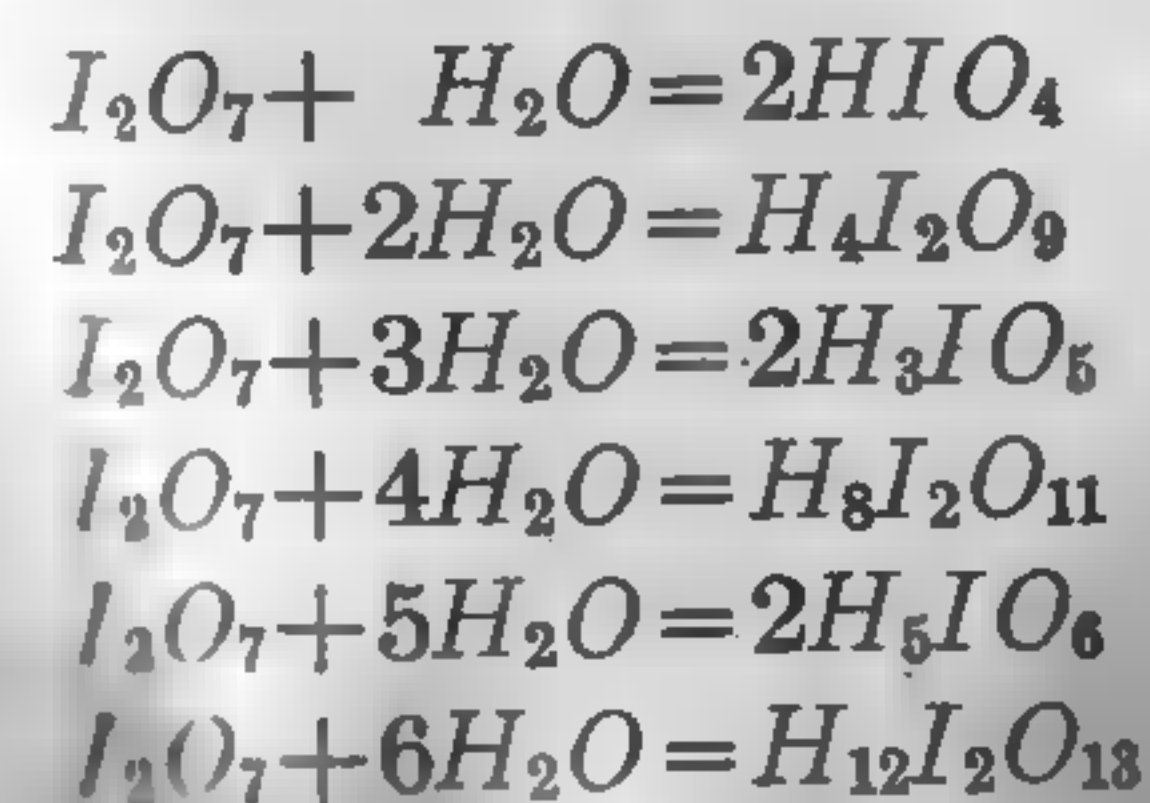


It is a solid crystalline body that fuses at $130^\circ C$, and decomposes at a higher temperature. Its salts are formed by oxidizing or heating iodates. The simplest way to prepare a periodate is to lead chlorine into a solution containing sodium hydrate and sodium iodate, when the following reaction takes place:



The salt $Na_2H_3IO_6$ is evidently derived from the acid H_5IO_6 . From it the corresponding silver salt, $Ag_2H_3IO_6$, can be prepared; when this is treated with nitric acid it is converted into $AgIO_4$. This latter acid is normally given as periodic acid, and the compounds H_3IO_5 and H_5IO_6 , which contain 1 and 2, molecules of water, respectively, are called *hydrates*. The fact that salts derived from these acids are known, makes it appear probable that the oxygen and hydrogen are in the form of hydroxyl groups instead of in the form of water.

Periodic acid forms a remarkable series of salts which appear to be very complex, and correspond to the following formulas: HIO_4 , $H_4I_2O_9$, H_3IO_5 , H_5IO_6 . These acids are known as *metaperiodic acid*, *diperiodic acid*, *mesoperiodic acid*, and *paraperiodic acid*, respectively. Although salts having the formulas $M_nI_nO_{11}$ and $M_{12}I_2O_{13}$ have been described, they do not appear to be definite compounds. These are accounted for by the supposition of a hypothetical periodic anhydride, I_2O_7 , from which the various acids are obtained by the addition of varying molecules of water, thus:



These acids, therefore, can be considered as being hydrates of the normal or metaperiodic acid, HIO_4 . According to their manner of acting it is better to consider that the hydrogen and oxygen are present in them in the form of hydroxyl groups, and not as water.

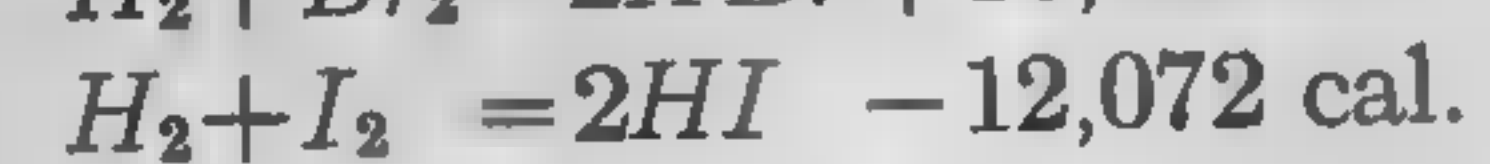
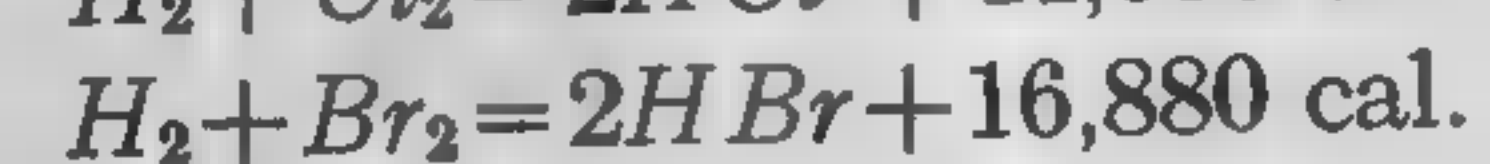
REVIEW OF THE HALOGENS

51. The elements fluorine, chlorine, bromine, and iodine form a closely allied group of non-metals known as the halogens. The connections between chlorine, bromine, and iodine are closer than with fluorine. Of these fluorine and chlorine are gases, bromine a liquid, and iodine a solid at ordinary temperature. The density of the series increases regularly with fluorine as the lowest and iodine the highest, while the chemical activity diminishes with increase in density. The stability of the hydrogen compounds of the halogens *decreases* as the density increases, but with the oxygen compounds it *increases* as the density increases. The usual method of preparing an acid is to treat a salt of that acid with a stronger acid, usually sulphuric acid. Hydrofluoric and hydrochloric acids are prepared in this way, but hydrobromic and hydriodic acids, on account of their instability, are more or less completely broken up by the sulphuric acid as fast as they are formed, and consequently cannot be obtained in this way. These two acids form the only notable exceptions to the general rule for preparing acids. Oxygen, which will not unite with fluorine, combines with iodine, forming the stable pentoxide, which requires a temperature of $300^\circ C$. for decomposition.

The relative affinities of these elements may be illustrated by using one of them to set another free from its compounds. Thus, if bromine is added to a solution of an iodide, it sets the iodine free, and is in turn set free from its compounds by the addition of chlorine. If chlorine is introduced into a solution containing an iodide and a bromide, it first sets the iodine free and forms the corresponding chloride. When all the iodine is set free, the chlorine begins to oxidize it at the expense of the water and converts it all into iodic acid before

any other reaction occurs. When all the iodine is converted into iodic acid, the chlorine sets the bromine free, and this colors the solution yellowish red.

52. The thermochemical relations of chlorine, bromine, and iodine with hydrogen may be shown by means of the equations:



That is, when 1 gram molecule (2 grams) of hydrogen unites with 1 gram molecule (70.36 grams) of chlorine, 2 gram molecules (72.36 grams) of hydrochloric acid is formed, and 44,000 calories of heat is liberated. Bromine also liberates heat, but not so much; and in the case of iodine the equation shows that when 2 grams of hydrogen unites with 252.02 grams of iodine, 254.02 grams of hydriodic acid is formed, and 12,072 calories of heat is absorbed. This is about as we would expect it to be from the relative stability of the compounds.

INORGANIC CHEMISTRY

(PART 5)

FAMILY 6, GROUP B

1. **General Remarks.**—Oxygen is really a member of Family 6, Group B, and as its atomic weight is the lowest, it would naturally be considered as the first member of the group. It has already been treated, however, and in this Section will be considered the other members of the group: sulphur, selenium, and tellurium. These three elements as well as the first occur in allotropic modifications. These three latter elements are much more closely related to one another than to oxygen. In fact, the relation is somewhat like that which chlorine, bromine, and iodine bear to fluorine. In general, their compounds have the same form as those of oxygen, but there are exceptions to this rule. For instance, they form compounds with oxygen, while oxygen forms no analogous compounds with them. Sulphur, selenium, and tellurium form with oxygen the compounds SO_2 , SeO_2 , and TeO_2 , but oxygen does not form similar compounds with these elements. That is, the compounds OS_2 , OSe_2 , and OTe_2 do not exist. The valence of these elements toward hydrogen is 2, as shown by the compounds H_2O , H_2S , etc.

Oxygen and sulphur also form the compounds H_2O_2 and (probably) H_2S_2 . But little is known of the constitution of this latter compound, and practically nothing of the valence of the sulphur in it. Toward the members of the halogen group the valence of these elements ranges from 2 to 6. Toward oxygen, the other three members of this group are quadrivalent and sexivalent.

Of these three elements, sulphur occurs in much the largest quantity, selenium comes next, and tellurium occurs in relatively very small amounts. Selenium frequently accompanies sulphur in nature, and tellurium often occurs in combination with gold and silver. Selenium and tellurium also occur together combined with gold and silver.

SULPHUR

Symbol S. Atomic weight 32.07. Density 32.07. Valence II, IV, VI. Specific gravity of native crystals 2.07. Molecular weight at 1,000° C. 64.14.

2. Occurrence.—Sulphur, one of the earliest known elements, occurs free and in a combined state throughout nature in the neighborhood of active and extinct volcanoes. Its compounds occur in nature in much larger quantities, and more widely distributed than the free sulphur itself. Combined alone with the metals it forms *sulphides* or *blendes*, and with metals and oxygen it forms *sulphates*. Compounds of sulphur are also found in the vegetable and animal kingdoms.

Sulphur forms an essential part of the animal tissues as a constituent of albumin, fibrin, etc., and it exists also, to a considerable extent, in the tissues of vegetables and plants; its compounds cause the peculiar odor of cruciferous and alliaceous plants, such as garlic, mustard, etc. It is found mostly in volcanic regions, those bordering on the Mediterranean being particularly rich in it. The present chief source of supply is Sicily, which furnishes about 80,000 tons annually. It is there found in large beds of blue clay both in an uncombined state and associated with magnificent crystalline masses of strontium sulphate. It has also been found in Iceland, New Zealand, Japan, Mexico, and many other localities. Within the last few years important deposits have been found in Louisiana.

The most important naturally occurring compounds of sulphur are:

Sulphides: Iron pyrites, FeS_2 ; galena, PbS ; blende, ZnS ; cinnabar, HgS ; stibnite, Sb_2S_3 ; realgar, As_2S_2 ; orpiment, As_2S_3 ; copper pyrites, $CuFeS_2$.

Sulphates: Gypsum, $CaSO_4 \cdot 2H_2O$; heavy spar, $BaSO_4$; green vitriol, $FeSO_4 \cdot 7H_2O$; Glauber's salt, $Na_2SO_4 \cdot 10H_2O$; Epsom salts, $MgSO_4 \cdot 7H_2O$.

3. Preparation.—Commercial sulphur is the native material in a purified state; the native sulphur is commonly distributed in veins through masses of gypsum and celestine, which must be separated from the sulphur by heat. This is accomplished by placing the native material in a row of earthen jars *A*, Fig. 1, heated by a long furnace, and provided with narrow tubes that convey the sulphur vapor into a second row of jars *B* that, standing outside of the furnace, act as receivers and condense the sulphur vapor into the liquid state, and from which it flows into vessels of water.

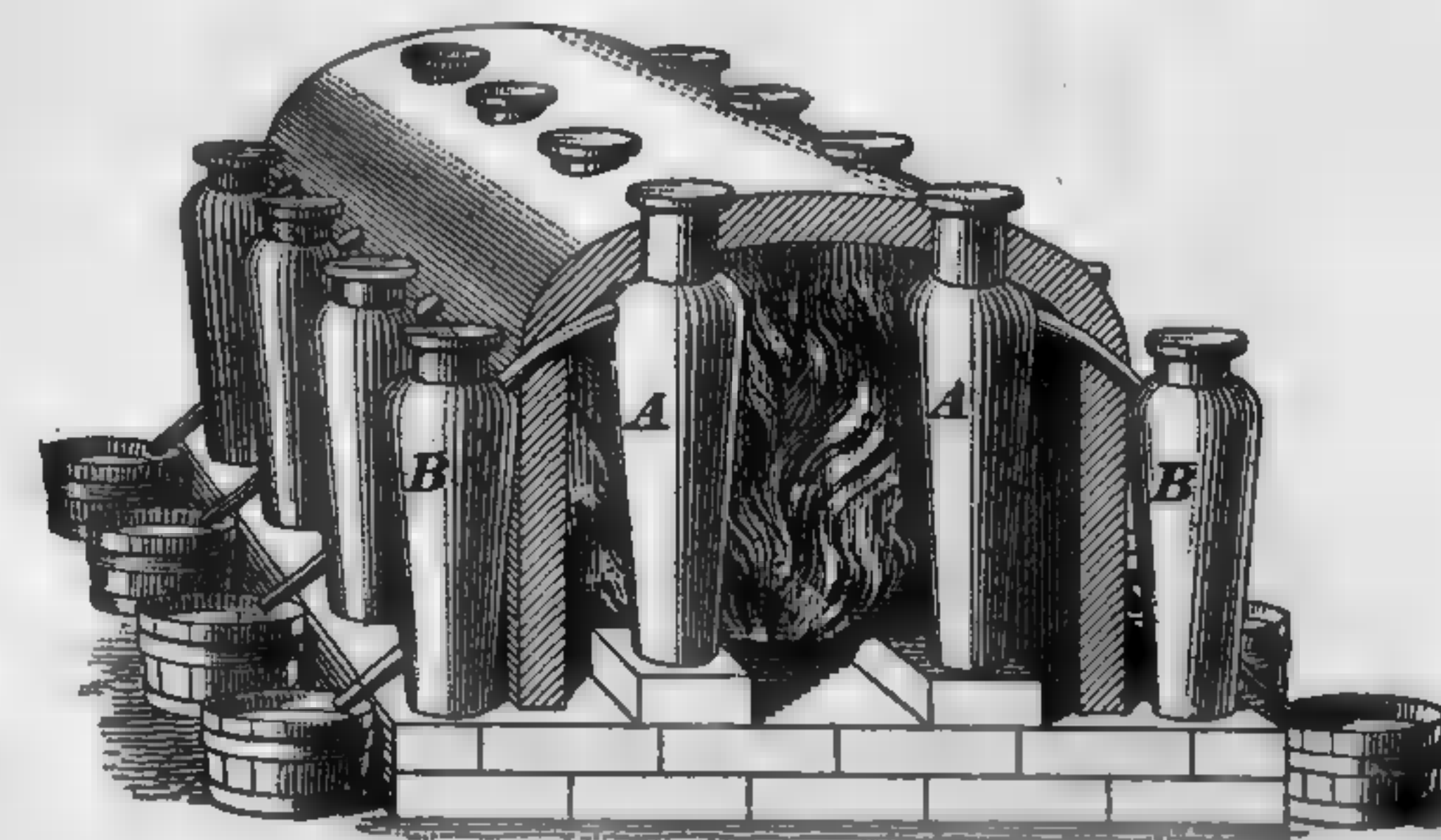


FIG. 1

The sulphur thus obtained is exported as *rough sulphur*, and contains between 3 and 4 per cent. of earthy impurities, which must be removed by distillation. This redistilling, or refining process, is done in the apparatus shown in Fig. 2. A cast-iron cylinder *A* receives the melted sulphur from a tank *C* which is heated by the waste gases of the furnace. The sulphur vapor enters a large brick chamber *B*, the floor of which is slightly inclined, so that the condensed liquid sulphur may flow toward a tap *H*, which can be opened when necessary. A damper *R*, which is regulated by a chain, permits the closing or opening of the cylinder *A*. The brick chamber *B* is provided with a safety valve *K*, which permits the escape of the expanded air.

At first, when the walls of the brick chamber are cold, the sulphur vapors condense in the form of a fine powder, known as *flowers of sulphur*; but when the walls of the chamber become thoroughly heated, the sulphur vapors condense to a liquid, which, on the tap *H* being opened, is drawn into a vessel *E* and ladled into cylindrical molds, where it soon solidifies and forms the commercial product commonly known as *brimstone*.

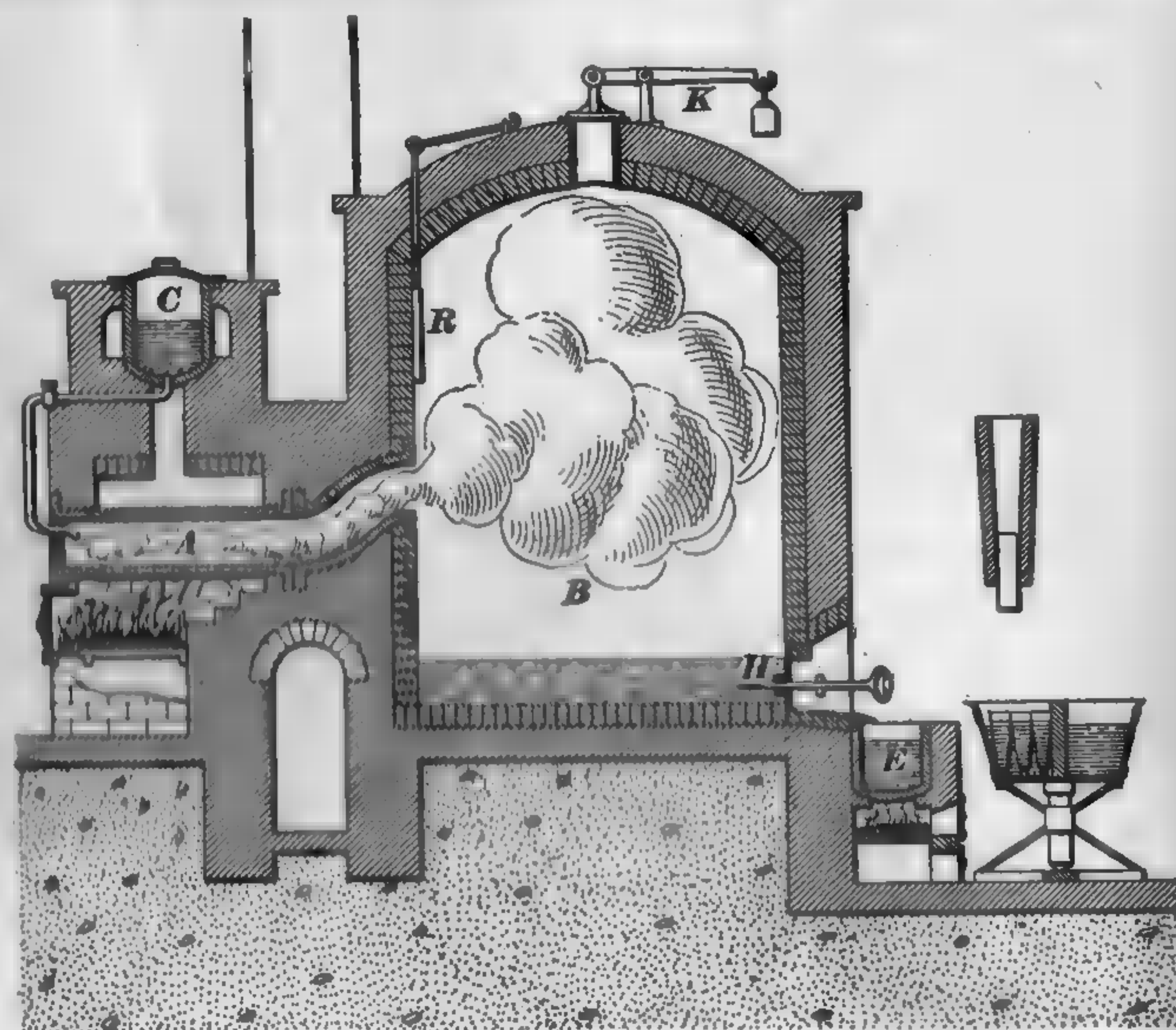


FIG. 2

In Sweden, Germany, and France sulphur is obtained by distilling iron pyrites. This method depends on the following decomposition of iron pyrites:

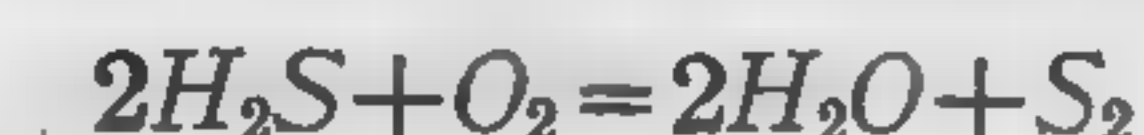


This decomposition is usually effected in a kiln, similar to a lime kiln, having an opening in the side into which a wooden trough is fastened. A small quantity of fuel is lighted on the bars of the furnace, and the kiln is filled with the pyrites. The burned pyrites is removed from time to time from the bottom, and fresh material is added on top. About half of the sulphur burns away and the rest is volatilized.

A more important source of sulphur is the residue or waste in the manufacture of soda. This waste material consists of calcium sulphide mixed with lime, chalk, and some alkali sulphides. The waste is treated with carbonic-acid gas in the presence of water, when hydrogen sulphide and calcium carbonate are formed:



The gas thus obtained is brought into contact with heated ferric oxide, when the following reaction takes place:



The sulphur formed is condensed in cooling chambers and recovered in a pure state.

4. Properties.—In its ordinary form, sulphur has a characteristic lemon-yellow color; it is insoluble in water; it may be called tasteless, but possesses a faint odor. Its rolls are extremely brittle; as it is at the same time a very bad conductor of heat, the warmth of the hand is frequently sufficient to cause the roll to fall in pieces when held. This phenomenon may be explained by the fact that roll sulphur, when freshly made, consists of a mass of oblique prismatic crystals, but, after being kept for some time, it consists of octahedra. This change in the structure of the mass, taking place when its solid condition prevents the free movement of the particles, gives rise to a state of internal tension and causes this extreme brittleness. The warmth of the hand causes an unequal expansion of the roll of sulphur; or, in other words, it causes an increased movement of its particles in that part of the roll that is directly exposed to the human heat, which results in a breaking up of the mass.

Sulphur melts at a temperature of 114.5°C . to a limpid, yellow liquid, which, if allowed to cool slowly, deposits long, prismatic, needle-like crystals. These are at first perfectly transparent, but after a short time become entirely opaque, through each breaking up into a number of minute rhombic octahedral crystals. Though the external form is retained, little coherence remains.

If sulphur is dissolved in carbon disulphide and the liquid allowed to evaporate, the sulphur is obtained in octahedral crystals of the rhombic system. These are permanent in air, and the form is that in which the native sulphur crystals occur.

EXPERIMENT 1.—Fill an iron ladle, or a clay crucible about $3\frac{1}{2}$ inches high, with sulphur, and heat it very gently over a small flame, taking care that the sulphur and the flame do not come in contact. As soon as the whole of the sulphur is melted, remove the Bunsen burner; as it cools, a crust forms over the surface, crystals being seen to shoot out from the side. As soon as this crust is formed, bore two holes through it with a piece of red-hot iron wire close to the edges and opposite each other; pour out the sulphur that remains melted, and with a knife cut the upper crust and remove it. It will be noticed that the interior is one mass of long, transparent needles, or prisms. Set the mass aside for 5 or 6 days, when it will be observed that the crystals have entirely lost their transparency.

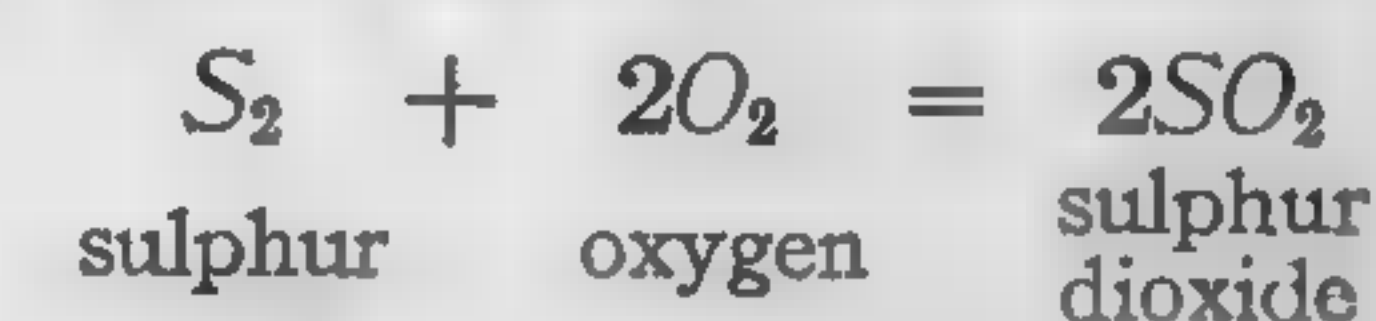
EXPERIMENT 2.—Shake up some flowers of sulphur with a little carbon disulphide, so as to form a saturated solution, in a test tube. Decant off the clear liquid and filter into an evaporating dish. Set aside and allow the carbon disulphide to evaporate spontaneously. A residue of more or less transparent octahedral crystals of sulphur will be found to remain in the dish.

5. These experiments prove that sulphur crystallizes in two distinct forms, the one from fusion, the other from solution. The latter is permanent, while the former is unstable and gradually changes into the latter. In addition, there is still another form, known as *plastic sulphur*, which possesses properties that differ widely from those of either. If, instead of allowing the limpid, yellow liquid produced by melting sulphur (obtained in Experiment 1 just before withdrawing the Bunsen burner) to cool, the application of heat is continued, a remarkable series of changes ensues. The color gradually darkens as the temperature rises; at the same time the liquid becomes thicker, until at a temperature between 200°C . and 260°C . the mass is almost black, and so viscid that the vessel may be inverted without the sulphur running out. With a further increase in temperature, the sulphur again becomes liquid, but remains of a much thicker consistency than it possessed when first melted. If, while in this state, it is poured into water, a soft, rubber-like, plastic mass is obtained. The

difference between this variety and the common brittle form of sulphur is very striking. In a few hours, however, it loses its tenacity and again becomes opaque and brittle.

Either variety of sulphur melts when heated to 114.5°C ., becoming always a yellow, limpid liquid. As the temperature rises it becomes viscid, until, between 200°C . and 250°C ., the vessel may be inverted without any of the sulphur running out; it then becomes liquid again, and at 448.4° it boils. The vapor density of sulphur was for a time considered anomalous, being at 500°C ., 192.42, until Bineau showed that at $1,000^{\circ}\text{C}$. it became normal (32.07) again. It was therefore assumed that at 500°C . the sulphur molecule must be hexatomic, while, if further heated to $1,000^{\circ}\text{C}$., it becomes normal (diatomic) again. Some recent experiments tend to show that the apparently greater vapor density at the lower temperature is due to imperfect vaporization of the sulphur, but this matter is uncertain at present.

When heated to 260°C . in the air, sulphur takes fire and burns with a pale-blue flame, emitting a suffocating odor; the reaction that takes place is represented by the equation:



Sulphur is a chemically active element, many metals taking fire readily in its vapor, and, burning actively, combine with it. It combines with silver at ordinary temperatures, giving the metal a black coating of silver sulphide.

6. Tests.—In the free state sulphur may be easily recognized by its color, its volatility when heated, and its characteristic odor when burned. Combined, as a soluble sulphide, by fusion with sodium carbonate and charcoal in a small closed crucible, it blackens paper moistened with a solution of lead acetate.

7. Uses.—Sulphur finds extensive employment in the arts and various manufacturing processes, such as the manufacture of sulphuric acid, gunpowder, in the vulcanization process of India rubber, for bleaching straws, woollens, etc.

8. Summary.—Sulphur is found in nature in volcanic districts, uncombined, and also combined as sulphides and sulphates. It is purified by distillation, is a lemon yellow, brittle solid; occurs in two crystalline forms, one of which is unstable; it may be obtained in the plastic form by the application of heat. It is volatile when heated and highly inflammable. It combines with most metals and with many of the non-metals.

9. Laboratory Directions.—To succeed in obtaining sulphur crystals by solidification of the melted body (see Experiment 1, Art. 4), bore the holes through the crust as soon as it forms, and drain the melted sulphur completely.

In pouring sulphur from a test tube, there is danger of the tube being cracked unless its upper part is thoroughly heated. The safest plan is, before pouring, to boil the sulphur until the whole tube is filled with vapor; by this means the tube becomes uniformly heated and the danger of cracking is reasonably removed; be very careful, nevertheless, to hold the test tube so that, in the event of its breaking, none of the sulphur falls on the hand; boiling sulphur produces very painful and disagreeable burns. The liquid will probably take fire as it leaves the test tube; this, however, is of no importance. Should any fall on the bench, at once throw a little water on it.

HYDROGEN SULPHIDE

Formula H_2S . Molecular weight 34.086. Density 17. Specific gravity 1.18.

10. History and Occurrence.—Hydrogen sulphide, formerly known as *sulphureted hydrogen*, was discovered by Scheele in the year 1777. It occurs in certain volcanic gases, and is the essential constituent of the water of the so-called sulphur springs, among the best known of which are Sharon and Avon, in the United States; Harrowgate, in England; Aix-la-Chapelle in Germany; and Bagnières, in France. It is found in the gas of eggs and sewers, being produced by the decomposition of the albuminoids.

11. Preparation.—Hydrogen sulphide may be prepared by the direct union of its components; that is, by passing hydrogen into sulphur vapor.

EXPERIMENT 1.—Arrange a retort with its stem just dipping beneath the surface of the water in the pneumatic trough. Place some sulphur in the retort and heat to the boiling point. Withdraw the stopper from the tubulure of the retort, and insert a cork through which has been passed a glass tube of such a length as to nearly reach the surface of the melted

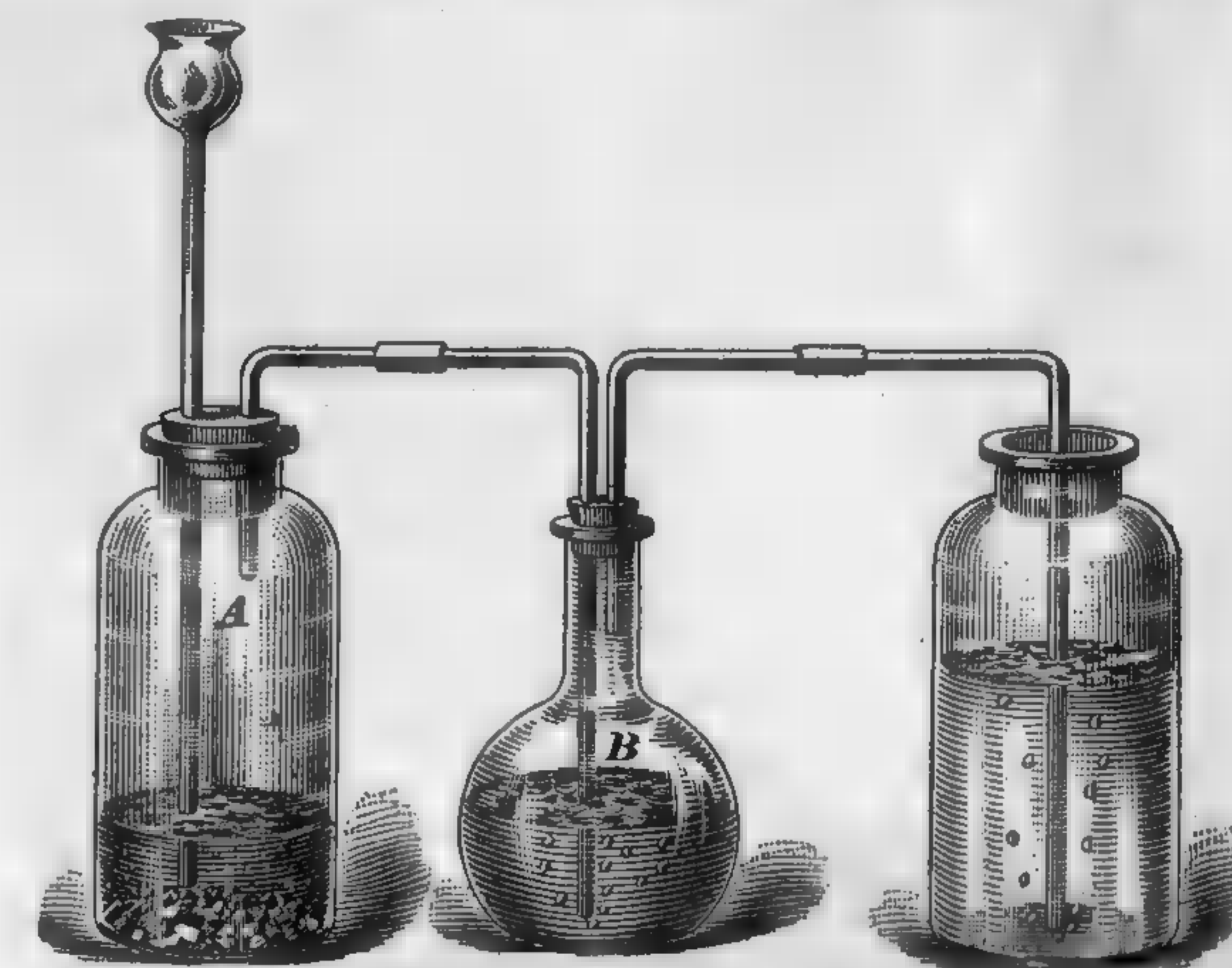


FIG. 3

sulphur. Through this tube pass hydrogen from a generating flask, and collect it as it escapes from the stem of the retort. The gas possesses the odor of rotten eggs, and a piece of paper moistened with a solution of lead acetate is blackened when plunged into it.

Hydrogen sulphide is prepared also by passing hydrogen gas over certain heated sulphides, such as antimony trisulphide:



It is usually prepared, however, by the action of dilute hydrochloric or sulphuric acid on metallic sulphides:



It is also formed when dilute acids act on a hydrosulphide:



In the laboratory the gas is generated by the action of either dilute hydrochloric acid or dilute sulphuric acid on ferrous sulphide.

EXPERIMENT 2.—A small quantity of iron sulphide is placed in the bottle *A* of the apparatus shown in Fig. 3. Dilute acid, about 1 part acid to 3 parts of water, is added through the funnel tube of *A* until the bottle is about one-third full. The gas is then conducted through the flask *B*, containing water to wash the gas, into a bottle or other vessel of water, or any other liquid on which the gas is intended to act.

When desired to stop the evolution of gas the acid is poured off, leaving the iron sulphide at the bottom of the bottle. If desired, the acid liquid can be set aside, when green crystals of ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, will form.

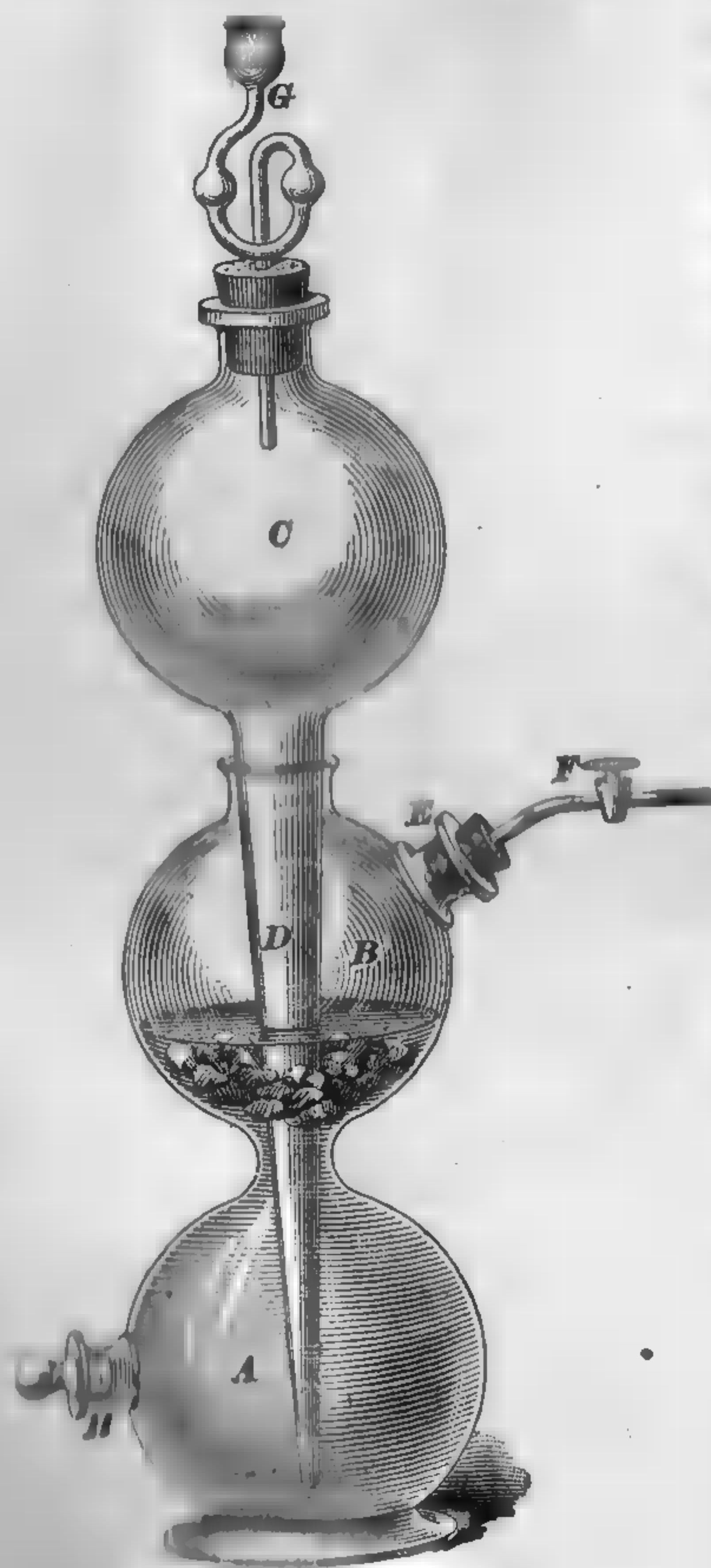


FIG. 4

neck of the second. Through the tubulure *E*, the ferrous sulphide, in fragments about the size of a chestnut, is introduced, the space between the tube and the side of the constriction being too narrow to let them drop into the bulb *A*.

12. For the continuous preparation of hydrogen sulphide from ferrous sulphide and dilute sulphuric or hydrochloric acid, in the larger laboratories, *Kipp's apparatus*, shown in Fig. 4, is very convenient. It consists of three glass bulbs, the two lower ones *A* and *B* being in a single piece, and the upper one *C* prolonged by a tube *D* reaching to the bottom of the lower, being ground air-tight into the

This tubulure *E* is then closed by a stopper, through which a glass stop-cock *F* passes. The diluted acid (in the proportion of 1 part of acid to 9 parts of water) is poured through the opening *G* in the bulb *C*, and runs into the bulb *A*, and rises to overflow the iron sulphide in bulb *B*. If the stop-cock *F* is open, the evolved gas escapes; but when it is shut the pressure of the accumulating gas forces the liquid away from the sulphide down into the bulb *A*, and thence back into bulb *C*, thus stopping the action of further generating, and, at the same time, preserving a certain volume of hydrogen sulphide always ready when required. The acid, when saturated, is removed through the tubulure *H*.

13. Properties.—Hydrogen sulphide is a colorless gas, and has the odor of rotten eggs. It is heavier than air, having a specific gravity of 1.18. Cooled to -74°C ., or submitted to a pressure of 17 atmospheres at 10°C ., it condenses to a colorless liquid of specific gravity of .9, which freezes to an ice-like mass at -85°C . It is soluble in water, 1 volume of which dissolves 3 volumes at ordinary temperatures, and 4.37 volumes at 0°C . The solution has a taste corresponding to the odor of the gas. It is inflammable and a non-supporter of combustion; mixed with air in the proper proportions it is explosive. Its reaction with blue litmus paper is weakly acid. It is easily decomposed by a temperature of 400°C . It reacts with metals and their oxides to produce sulphides, setting hydrogen free in the first case and water in the second. In the form of a gas or in solution it is converted into water and sulphur by all oxidizing agents:

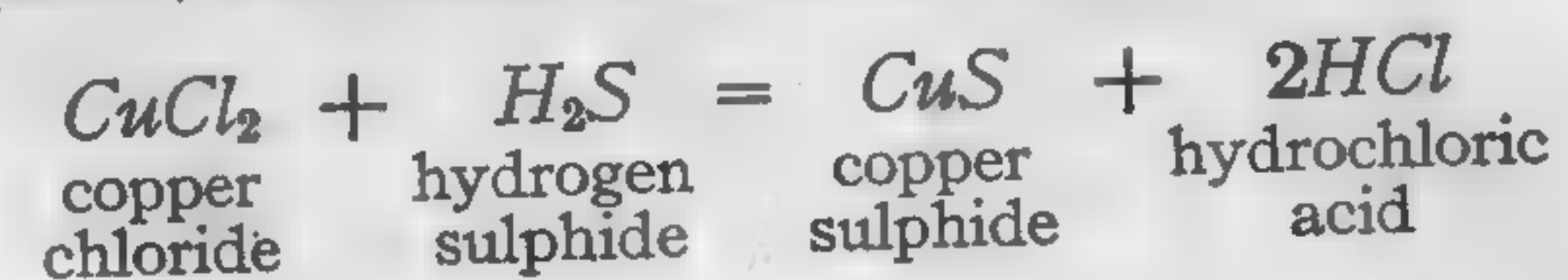


This property is also possessed by the halogens. The affinity possessed by hydrogen sulphide for oxygen enables it to remove the latter from its compounds, thus acting as a reducing agent. Hydrogen sulphide is exceedingly poisonous; according to Faraday, birds die in air containing but $\frac{1}{1500}$ part of it, and dogs in that which contains but $\frac{1}{1000}$.

14. Tests.—Hydrogen sulphide is easily detected by placing in it a piece of paper moistened with a solution of lead

acetate; in this way it may be shown to exist in most specimens of coal gas, and in the gaseous exhalations from drains, cesspools, etc. With sodium nitroprussiate in alkaline solution, it gives a deep-purple color.

15. Acidity of Hydrogen Sulphide.—The action of hydrogen sulphide on blue litmus paper shows that the gas possesses acid properties, hence it is often called hydrosulphuric acid. These are, however, so feeble that, in the case of soluble sulphides, carbon dioxide is able to displace the hydrogen sulphide. The sulphides of all the metals are insoluble in water, with the exception of those of calcium, barium, strontium, magnesium, sodium, and potassium, and a few of the very rare metals. The insolubility of the other metallic sulphides affords to the analyst a very valuable means of separating those metals from the above-mentioned group. Whenever the compounds are brought together which respectively contain elements that, by their union, are capable of forming an insoluble compound, that compound as a rule will be formed; so that, although hydrogen sulphide is rather a weak acid, it is able to displace stronger ones from many metals. A current of hydrogen sulphide passed through a solution of copper chloride precipitates copper sulphide, according to the equation:



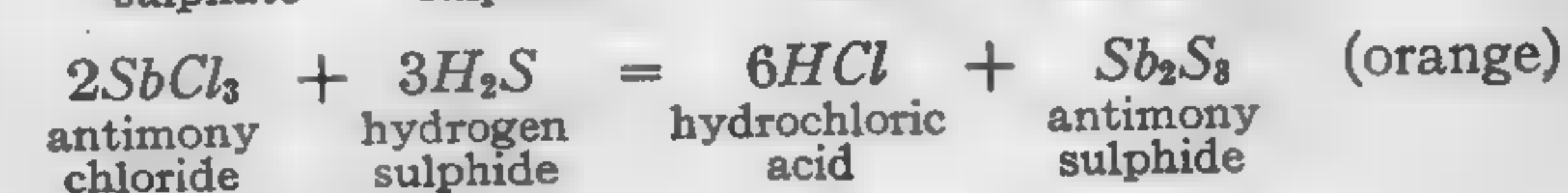
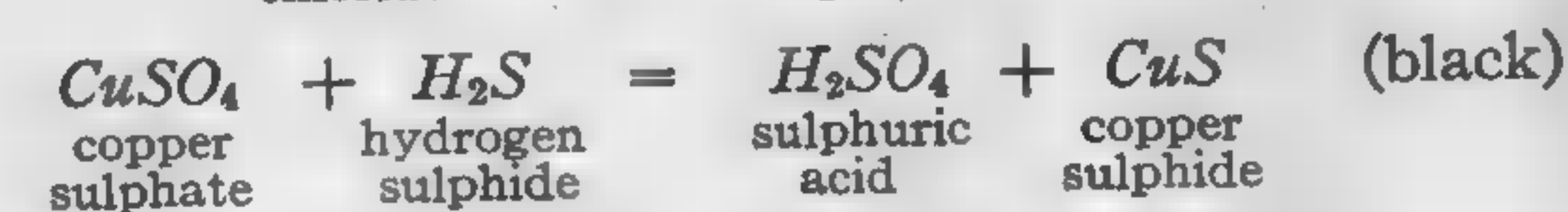
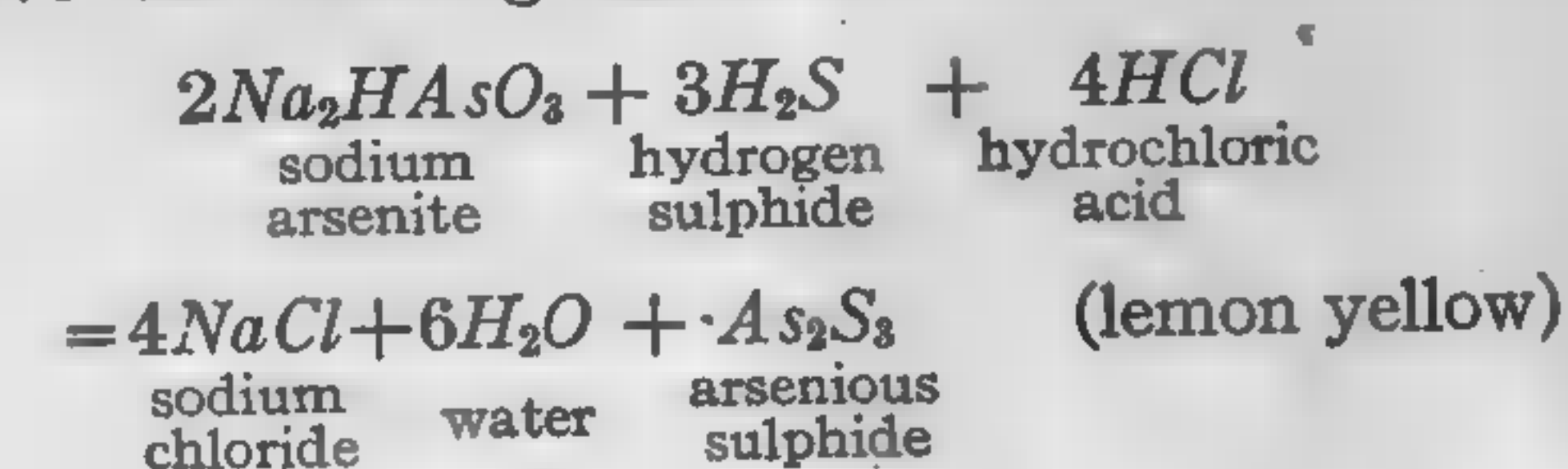
although hydrochloric acid is much more powerful in its action.

These sulphides have, in many cases, very characteristic colors, by which they may be readily recognized. They possess, further, the advantage of being divided into two distinct groups, namely, into one group that is soluble in dilute hydrochloric acid, and into one that is insoluble in this agent.

EXPERIMENT.—Prepare in separate test tubes a solution of sodium arsenite, copper sulphate, antimony chloride,* and zinc sulphate; acidulate these solutions by adding a few drops of hydrochloric acid to each, see that

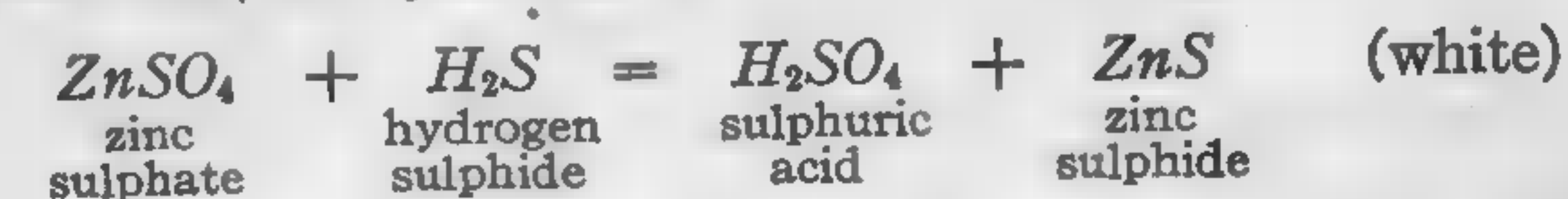
* Through hydrochloric acid must be added to this during solution to prevent the separation of an insoluble compound and keep the solution clear.

the solution turns blue litmus paper red, and pass hydrogen sulphide through each solution from the generating apparatus shown in Fig. 3. The leading tube of the generating apparatus that dips into the solution must be carefully washed each time it is changed from one solution to another. Observe the following reactions:



$\left. \begin{array}{c} \text{ZnSO}_4 \\ \text{zinc} \\ \text{sulphate} \end{array} \right\}$ In acid solution, H_2S produces no precipitate.

Introduce zinc-sulphate solution into a clean test tube, but do not add hydrochloric acid, and you will obtain the following result:



If you add to this a few drops of hydrochloric acid, you will find that the precipitate is immediately dissolved.

These experiments show that the sulphides thus produced are well-defined salts, and a series of bodies of great importance.

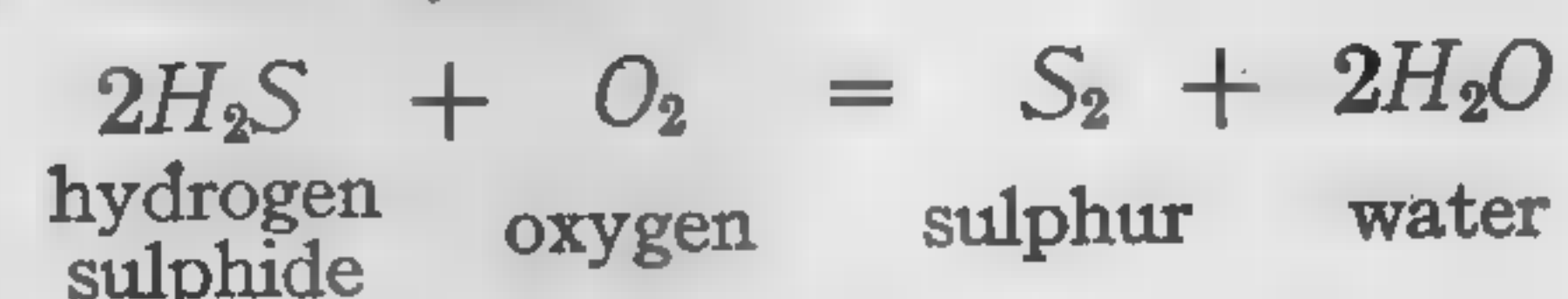
Compounds are also formed in which only 1 hydrogen atom of the H_2S is replaced by a metal. These have the general form MSH , and are known as sulphhydrates or hydrosulphides. Potassium hydrosulphide or sulphhydrate has the formula K—S—H . Although sulphur is able to displace the metals from their compounds with chlorine, yet chlorine is capable of decomposing hydrogen sulphide very readily, the action being:



16. Decomposition of Hydrogen Sulphide.—The existing great affinity between hydrogen and chlorine leads to the decomposition of hydrogen sulphide, as has been shown in the last equation in the preceding article.

Free oxygen has no action on the dry gas, but in the presence of water a slow oxidation takes place. Hence, an aqueous

solution of hydrogen sulphide becomes turbid on exposure to the atmosphere, through the separation of sulphur and the formation of water, thus:



17. Summary.—Hydrogen sulphide occurs free in the gases evolved from volcanoes, and combined in the waters of certain springs, known as sulphur springs. It is usually prepared by the action of sulphuric acid upon sulphides. It is soluble in water, is a colorless gas with the disgusting smell of rotten eggs, and is a non-supporter of combustion. Chlorine decomposes it. It possesses feeble acid properties; certain sulphides possess characteristic colors by which they may be readily recognized.

18. Laboratory Directions.—After the preparation of hydrogen sulphide, always wash out carefully the apparatus used before putting it away; otherwise, a mass of crystal of iron sulphate may form. Any iron sulphide remaining unused should be washed and dried, and then returned to its proper bottle or box. There is sometimes some difficulty, when sulphide is taken that has been previously used, in getting the action to commence; there should always be a little fresh sulphide added as well. The difficulty also sometimes arises through the sulphuric acid being too strong.

HYDROGEN PERSULPHIDE

19. Hydrogen persulphide was first prepared by Scheele and completely investigated by Berthollet. It is prepared by adding a clear, well-cooled solution of the alkali or alkaline earth polysulphides to dilute hydrochloric acid. Calcium pentasulphide is most commonly used in the preparation of this compound. It separates as a heavy, yellowish oil with an acid, unpleasant taste, a characteristic pungent smell, and a specific gravity of 1.7. It is almost insoluble in alcohol but dissolves readily in carbon bisulphide and in benzene. It decom-

poses slowly when dry and away from the air into hydrogen sulphide and free sulphur. Water and heat hasten the decomposition.

OXIDES AND ACIDS OF SULPHUR

20. Sulphur forms the following series of oxides and acids:

Sulphur dioxide, SO_2	Hyposulphurous acid, H_2SO_2
Sulphur trioxide, SO_3	Sulphurous acid, H_2SO_3
	Sulphuric acid, H_2SO_4

HYPOSULPHUROUS ACID

21. Hyposulphurous acid, H_2SO_2 , or *dithionous acid*, has been obtained by a German chemist named Schützenberger, by the reduction of sulphurous acid by means of zinc, according to the equation:



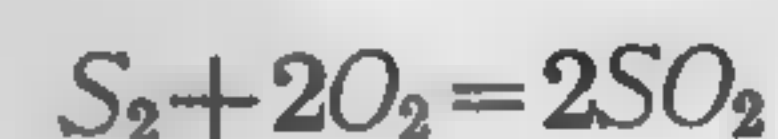
A yellow solution resulted that possessed a strong bleaching power, decolorizing litmus and indigo solutions readily. The acid combines readily with oxygen and is a more active reducing agent than sulphurous acid. It is decomposed on standing in the air, producing sulphurous acid, water, and sulphur.

SULPHUR DIOXIDE

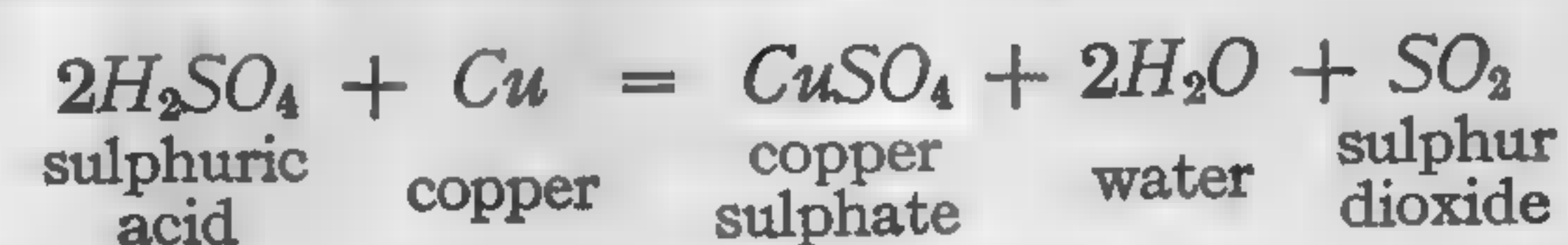
Formula SO_2 . Molecular weight 64.07. Density 31.83.

22. History and Occurrence. Attention was first called to sulphur dioxide by the alchemist Stahl, but not until 1774 did Priestly carefully investigate this compound and its properties. In nature, sulphur dioxide is but rarely met with; it exists, however, in the gases issuing from volcanoes. Although constantly discharged into the air of towns by the combustion of coal (which always contains more or less sulphur), it is so easily oxidized and converted into sulphuric acid that no considerable quantity is ever found in the atmosphere.

23. Preparation and Properties.—Sulphur dioxide is uniformly the product of the combustion of sulphur in air or in pure oxygen, being formed thus:



When needed for laboratory use it is generally prepared by heating sulphuric acid with metallic copper:



EXPERIMENT 1.—Twenty grams (about $5\frac{1}{2}$ cubic centimeters according to your measuring glass) of copper clippings is heated in a Florence flask with 110 cubic centimeters of strong sulphuric acid, the gas being conducted by a bent tube down to the bottom of a dry bottle closed with a perforated card. Some time will elapse before the gas is evolved, for sulphuric acid acts upon the copper only at a high temperature; but when the evolution of the gas fairly commences it will proceed very rapidly, so it is necessary to remove the flame from under the flask. The gas will contain a little suspended vapor of sulphuric acid, which makes it turbid.

Pure sulphur dioxide is also prepared by treating a sulphite with dilute sulphuric acid, thus:



and also by heating together sulphuric acid and sulphur:



On a large scale it is prepared by heating carbon and sulphuric acid together. Carbon dioxide is also evolved, but this is not detrimental when the sulphur dioxide is used for the manufacture of sulphites. The equation governing this reaction is:



In the manufacture of sulphuric acid the main source of sulphur dioxide is the burning of iron pyrites.

Sulphur dioxide is a very heavy, colorless gas, with a pungent, suffocating odor, resembling the odor of a burning sulphur match. It is more than twice as heavy as air, its specific gravity being 2.23. Cooled to -10° C. it condenses to a thin, colorless liquid, with a specific gravity of 1.49; this liquid freezes

at -76° C. The dry gas is incombustible in the air, does not support combustion, and does not have an acid reaction with litmus. In the presence of water, however, it has a decided acid reaction toward litmus. The gas is somewhat poisonous, due to the absorption of sulphur dioxide by the blood, with subsequent oxidation to sulphuric acid. The moist gas is a strong bleaching agent. It is quite soluble in water and its solution dissolves phosphorus, sulphur, iodine, bromine, and many gases. Sulphur dioxide has a great affinity for oxygen and is slowly oxidized to sulphur trioxide:



24. Tests.—Sulphur dioxide when free is at once detected by its pungent odor, and by its blackening action on paper moistened with a solution of mercurous nitrate. In combination as a sulphite, it evolves hydrogen sulphide when added to any solution evolving hydrogen. Another test for sulphur dioxide is the blue color obtained on paper moistened with a solution of potassium iodate and starch when brought into the gas.

25. Summary.—Sulphur dioxide is emitted from volcanoes, and is prepared by the action of copper on sulphuric acid. The gas has a pungent odor, is colorless, and may be easily condensed to a liquid by cold. It is very soluble in water, its solution being acid to litmus, and contains sulphurous acid, which forms a series of salts known as sulphites. It acts as a bleaching and disinfecting agent.

26. Laboratory Directions.—In inserting copper filings in a Florence flask, take care that they do not drop through the bottom; the best plan is to hold the flask in a horizontal position and slide them slowly in.

In heating sulphuric acid, be very careful to use every precaution to prevent the cracking of the flask; for instance, never allow the flame to play directly on the glass; always place a piece of wire gauze between the flask and the flame; keep the flame rather small. Never hold the hands where there is any danger, in event of a breakage, of the hot acid running on them.

Should, however, such a misfortune, by any accident, happen, immediately place the burned part under a continuous stream of cold water for at least 10 or 15 minutes, and then have the hand dressed by a physician.

To make a freezing mixture, mix 2 parts of ice and 1 part of salt.

SULPHUR TRIOXIDE

Formula SO_3 . Molecular weight 80.07. Density 39.73.

27. Preparation.—Sulphur trioxide, or *sulphuric anhydride*, is prepared by passing a mixture of sulphur dioxide and oxygen over heated platinum sponge. Platinized asbestos may be used in place of the pure platinum sponge. The apparatus

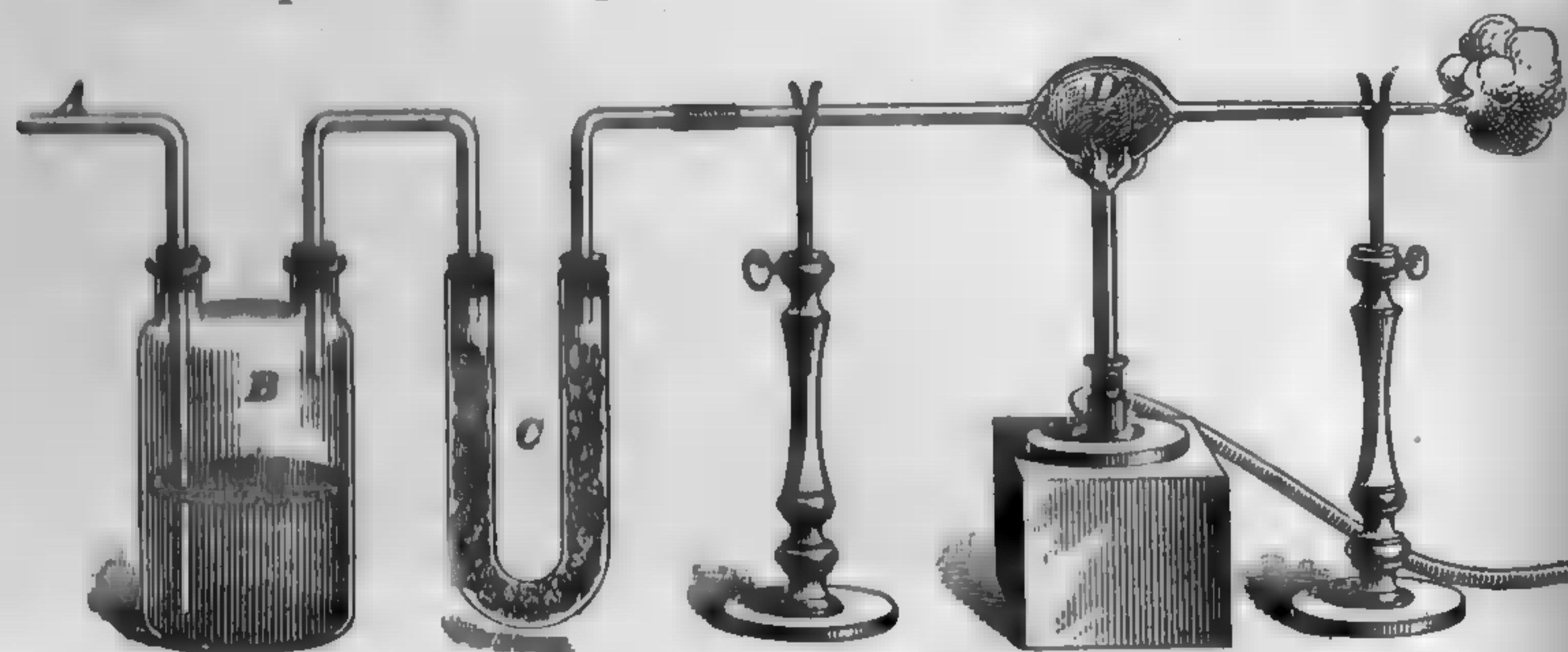


FIG. 5

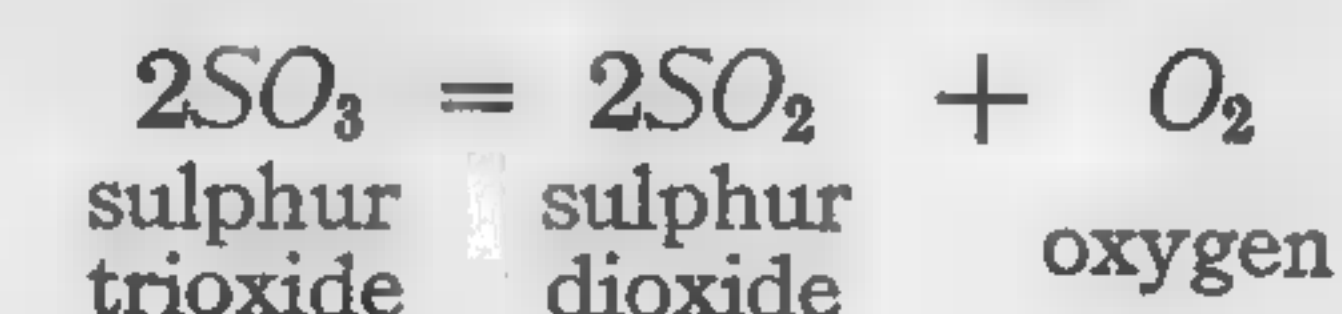
shown in Fig. 5 may be used to show the preparation of sulphur trioxide from sulphur dioxide. Oxygen is led through the tube *A*, through a strong solution of sulphurous acid contained in *B*. Here the oxygen takes up sulphur dioxide and the mixture is passed through pumice stone in *C* soaked with sulphuric acid to remove all traces of moisture from the mixture, and then passed over the heated platinized asbestos in *D*.

Sulphur trioxide can be formed also by passing a mixture of sulphur dioxide and air over heated copper oxide, ferric oxide, or chromic oxide.

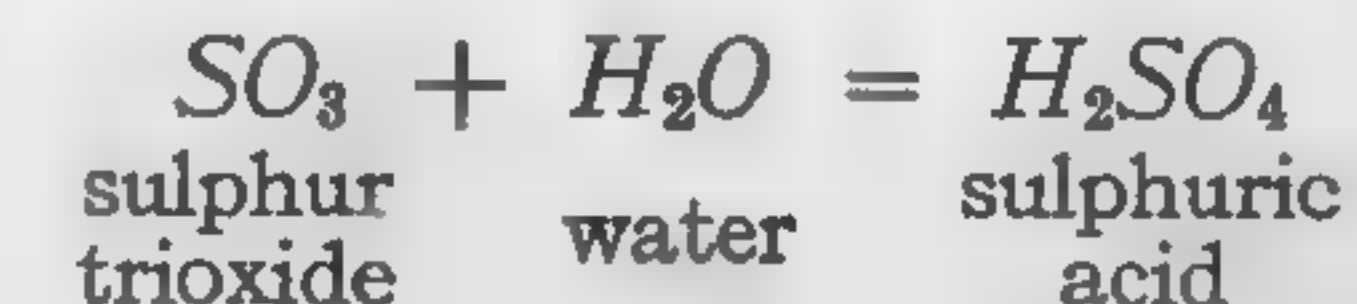
It can be prepared very conveniently by distilling fuming (Nordhäuser) sulphuric acid. The acid is heated gently in a retort, the trioxide being collected in a perfectly dry well-cooled receiver.

28. Platinized asbestos may be obtained by wetting some asbestos with solution of platinic chloride and heating this to redness, whereby the platinum is reduced to the metallic state, thus covering the asbestos with a thin film of platinum.

29. Properties.—Sulphur trioxide exists in two polymeric modifications. The β is a wax-like, white solid that crystallizes in silky fibers resembling asbestos, and on heating to $50^\circ C$. is converted into the α variety. It has a specific gravity of 1.9 and melts at $14.8^\circ C$. and boils at $46^\circ C$. When purified by repeated distillation in hermetically sealed tubes, it changes into a colorless liquid. Its chemical activity is greater than that of the β modification. On passing sulphur trioxide through a red-hot tube, it is separated into oxygen and sulphur dioxide.



Sulphur trioxide unites readily with water, with the evolution of great heat, producing sulphuric acid.



SULPHURIC ACID

Formula H_2SO_4 . Molecular weight 98.086. Specific gravity of liquid at $0^\circ C$. 1.84. Boiling point $338^\circ C$.

30. History and Occurrence.—The discovery of sulphuric acid dates back more than four centuries; it was first prepared by an alchemistically inclined monk, Basil Valentine, in the 15th century, who called it "*oleum sulphuris per campanum*." Doctor Roebuck, an Englishman, proposed the present method of manufacture in 1770. The acid thus prepared is therefore often called *English sulphuric acid*.

Sulphuric acid occurs free to a remarkable extent in river and spring waters. Boussingault, a French chemist, estimates that the Rio Vinagre, in South America, carries daily to the sea more than 38,000 kilograms; and that the water of

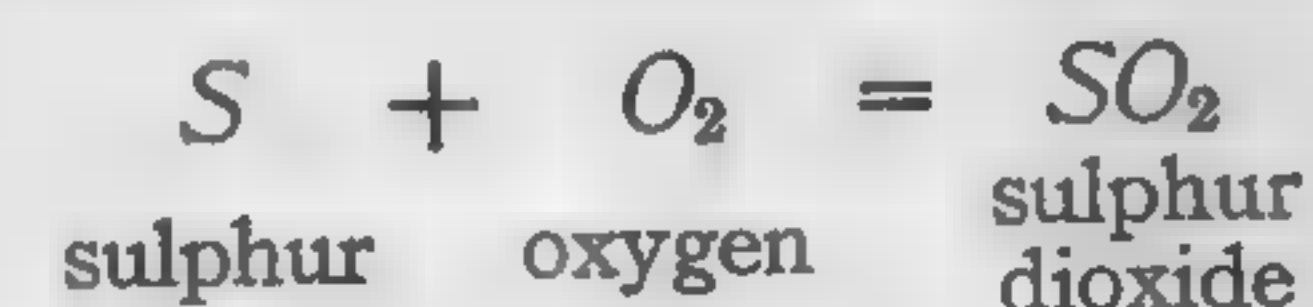
the Oak Orchard mineral spring, New York, contains, in each liter, about 2.5 grams.

Not only is it found in water, but also in the animal and mineral kingdoms. It has been observed as a secretion of certain mollusks, and is found in the sulphates of iron, calcium, barium, and strontium, forming the minerals melanterite, gypsum, barite, and celestite.

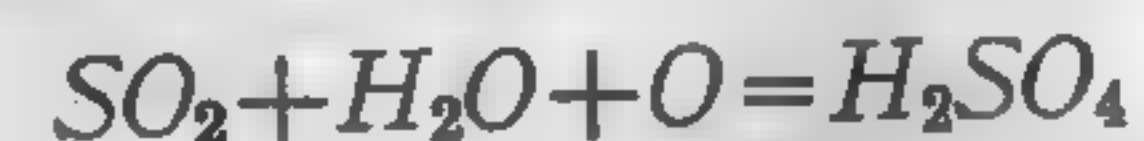
31. Importance of Sulphuric Acid.—There is no substance, with the single exception of water, that is so important to the chemist, be he manufacturing or analyzing, as sulphuric acid. The frequency of its application to various purposes in the preceding experiments will give some idea of its usefulness and a familiarity with its appearance, properties, etc.

32. Preparation.—Sulphuric acid is manufactured on an immense scale in this country as well as in England, and is never prepared in the laboratory for actual use, but always bought. A detailed description of the present process of manufacture will be very easily understood after a consideration of the principles of the chemical changes on which it depends.

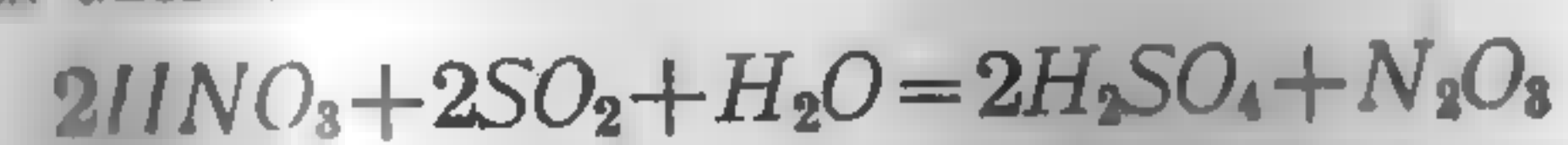
Sulphur dioxide is produced by burning sulphur in the air, thus:



When sulphur dioxide is treated with an oxidizing agent in the presence of water it is converted into sulphuric acid, thus:

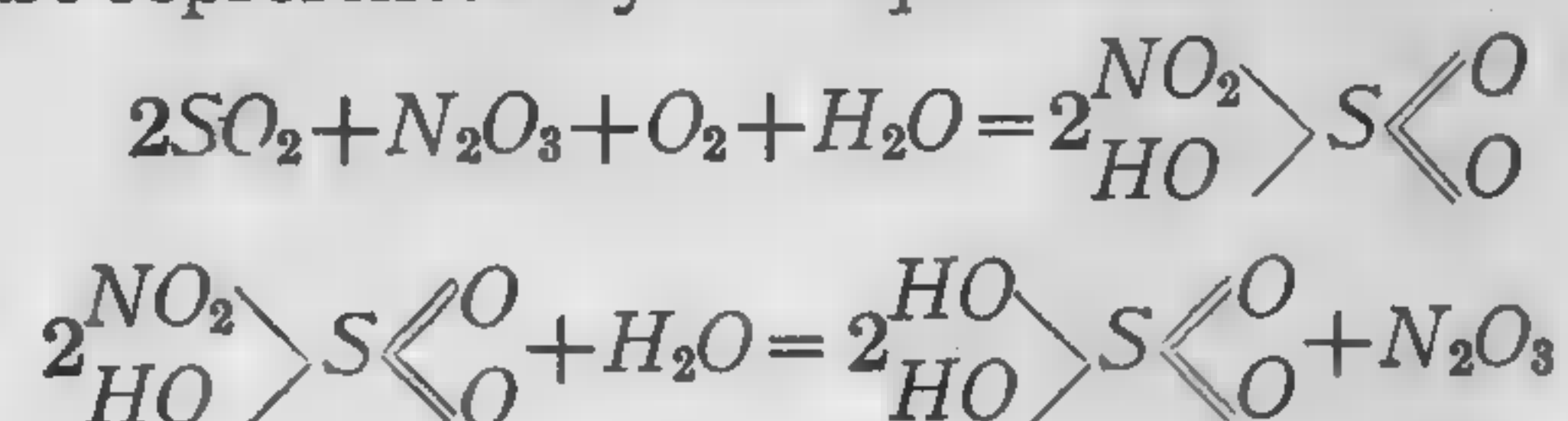


In practice the oxidation is principally accomplished by a mixture of nitric oxide and nitrogen peroxide, NO and NO_2 , which acts like nitrogen trioxide, N_2O_3 , and is so written in the following equations. In starting the process, nitric acid is used as the oxidizing agent instead of nitrogen trioxide. The reaction is as follows:



After this the oxidation is accomplished principally by N_2O_3 , and the principal reactions are the formation of nitrosyl

sulphuric acid, NO_2OHSO_2 , and the decomposition of this compound by water with the formation of sulphuric acid. These reactions are represented by the equations:



The nitrogen trioxide formed in the second reaction serves to oxidize a second portion of sulphur dioxide, so that theoretically a small quantity of this gas should be capable of

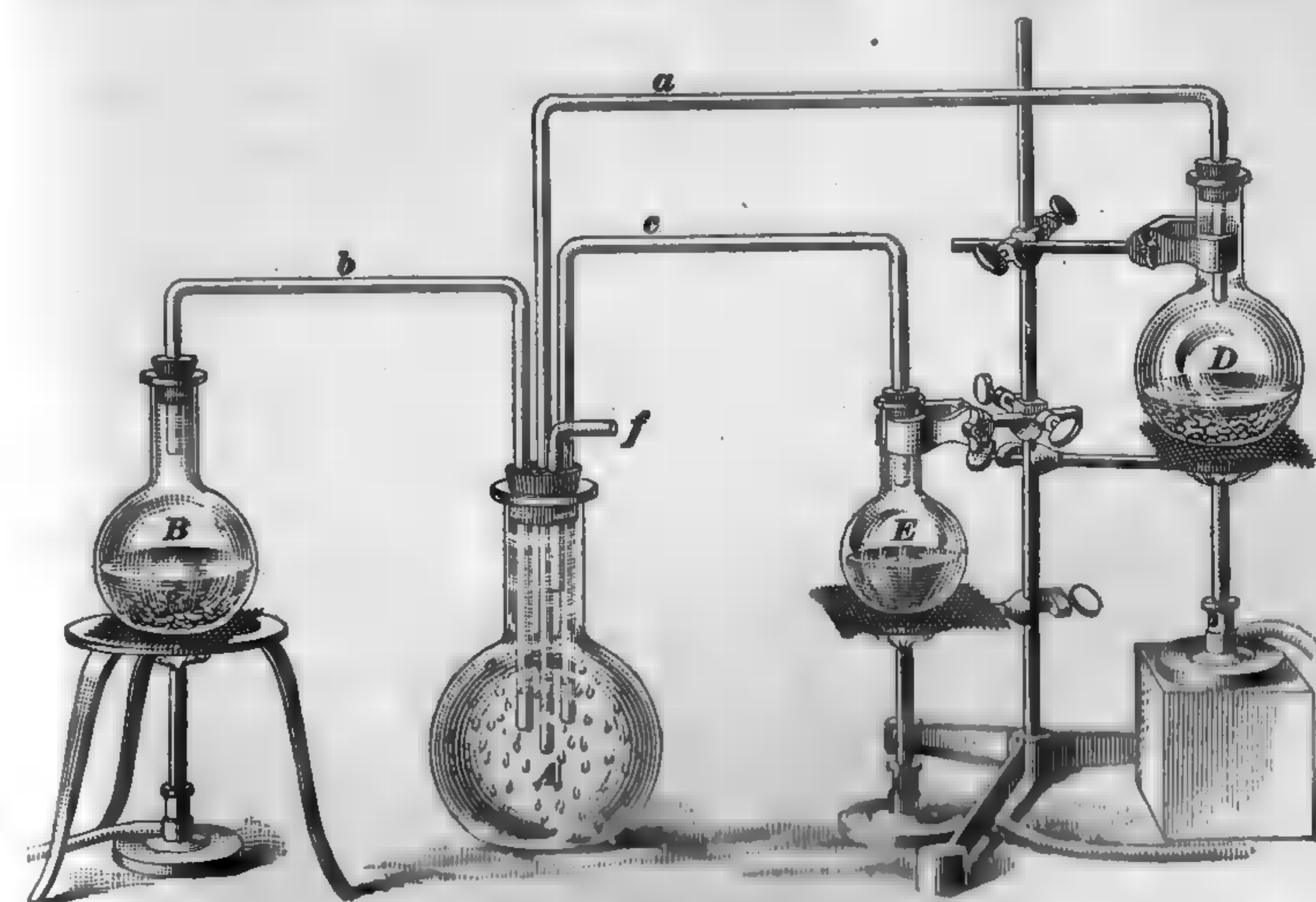


FIG. 6

oxidizing an indefinite quantity of sulphur dioxide, and in modern plants the waste of nitrogen trioxide is but slight.

The chemical principles illustrating the manufacture of sulphuric acid are shown in Fig. 6 and will aid in giving a clear understanding of the process employed in manufacturing sulphuric acid on a large scale.

A large Florence flask *A*, Fig. 6, is fitted with a stopper, through which pass several tubes: a tube *a* connected with a flask *D* containing copper and strong sulphuric acid for evolving SO_2 ; a tube *b* connected with the flask *B* containing copper

and dilute nitric acid for supplying nitrogen dioxide; a tube *c* connected with a small flask *E* containing water; a tube *f* for supplying air and preventing the pressure in *A* rising above that of the atmosphere. On heating the flask *B* nitric oxide passes over in flask *A*, combines with oxygen of the air and

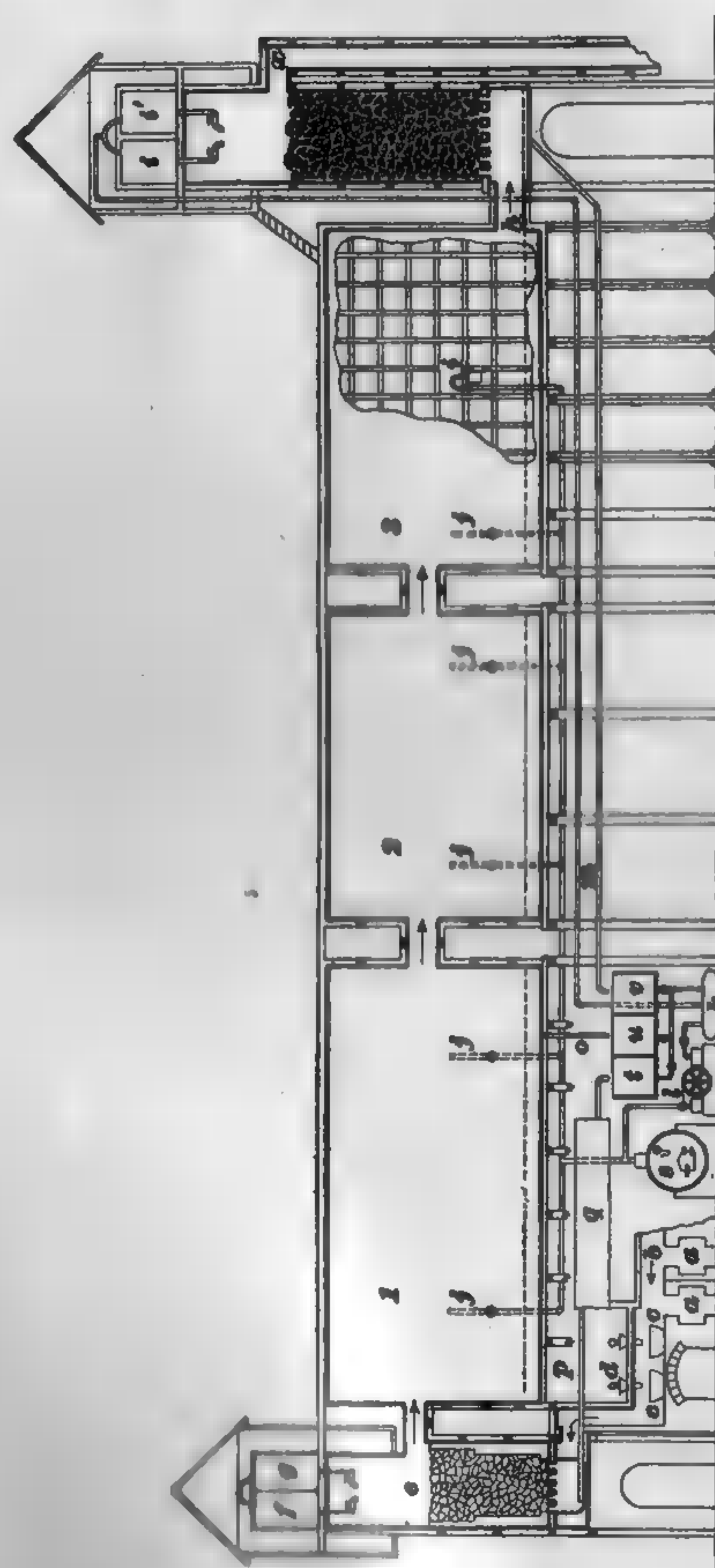


FIG. 7

changes to nitrogen peroxide and nitric oxide. Flask *D* is then heated, when sulphur dioxide is evolved. This passes over into *A* and decolorizes the red gas. The heat is then removed from *D* and steam is generated in flask *E* and sent into *A*, the nitrosyl sulphuric acid being decomposed and sulphuric acid formed.

33. The manufacture of sulphuric acid on a large scale is as follows:

Sulphur dioxide is produced by burning sulphur, or, more cheaply, by roasting sulphur ores (mostly iron pyrites), in a suitable furnace, by which a mixture of air and sulphur dioxide is obtained. The reaction

between the various bodies then occurs in large chambers made of timber framing and lined with sheet lead, the joints being made air-tight by melting the edges together.

Fig. 7 shows the general arrangement of a modern English sulphuric-acid works; *a, a* are two of a series of pyrite burners

generating SO_2 , which, passing along the flue *b*, heats the cast-iron troughs *c*, which are supplied with sodium nitrate and sulphuric acid through the funnels *d* for the production of nitric-acid fumes, which together with SO_2 proceed onwards to the Glover tower *e*. This tower consists of a framework of timber supporting a column of thick sheet lead, and lined with a wall of refractory bricks built without mortar and diminishing in thickness toward the top. The remaining space is filled either with large flints or with reticulated, or "pigeon-holed," brickwork, through the interspaces of which the gases pass upwards, meeting on their way sulphuric acid trickling downwards from the tanks *f* and *g* on the tower top, and so reach the first leaden chamber *1*, which consists, as has been already explained, of a timber framework lined with lead and supported on cast-iron pillars. Into this chamber steam from the boiler *s* is introduced by the jets *j* set in the side of the chamber. Here the characteristic sulphuric-acid reaction occurs, and the acid collects on the bottom of the chamber, which, for this purpose, has been shaped like a huge saucer.

In the first chamber most of the SO_2 is converted into H_2SO_4 and the remaining gases, in which oxides of nitrogen begin to predominate, pass to a second chamber *2*, where they again meet steam, and a further precipitation of sulphuric acid takes place, leaving the remaining gases still richer in nitrogen compounds and poorer in sulphur dioxide and acid to pass into the next chamber *3*, where nearly the whole of the SO_2 is converted into liquid H_2SO_4 . The remaining gases, which, theoretically, should now only consist of residual nitrogen, a necessary excess of oxygen, oxides of nitrogen, and a trace of sulphur dioxide, pass from this chamber by the flue *h* to the Gay-Lussac, or absorbing, tower, which consists of a timber framework lined with lead, inside of which is built a wall of bricks without mortar. The inside space of this tower is filled with hard coke, down which sulphuric acid (specific gravity 1.75) trickles from the cisterns *i, i'*. This acid meets and absorbs the nitrogen oxides from the escaping gases, leaving only the excess of air, the atmospheric nitrogen corresponding to the oxygen taken up in the reactions, and a minute trace of SO_2 . These

pass from the tower by the exit flue x to the chimney of the works, which produces the draft for the apparatus, their escape being regulated by a damper not shown in the figure. The number of chambers in a series varies from two to six in different works; their shape and size also vary within certain limits, the average size being 100 ft. \times 20 ft. \times 20 ft.

It now only remains to explain the workings of the towers. Sulphuric acid of a specific gravity of 1.75 is run from the cistern t containing strong acid into a closed cast-iron vessel k , known as the *egg*. When the egg is filled, the valve communicating with the cistern is closed, and a valve is opened that connects the egg with a powerful air-pumping engine l , that, working at a pressure of 60 pounds per square inch, forces the acid out of the egg, up the pipe m into the cisterns i, i' , at the top of the absorbing tower, whence it slowly trickles down through the coke, taking up the nitrogen compounds, and running by way of the pipe below m to the cistern v , whence, as required, it is run into the egg and forced through a pipe similar to m , but not shown in the figure, to the cistern f on top of the Glover tower. The acid made in the chambers, and which possesses a specific gravity of 1.6, is drawn from time to time by pipe o into the so-called *chamber-acid* cistern u , from which it is blown into cistern g on the Glover tower. The run of nitrogen containing acid from cistern f and of chamber acid from cistern g is so adjusted that, after trickling down the hot flints or bricks and meeting the hot mixture of gases on its way through the tower, the acid runs off by the pipe p . Deprived of its nitrogen compounds, which enter the chambers, and concentrated by the heat to a specific gravity of from 1.73 to 1.75, it passes through a coil of lead piping immersed in cold water (in the cooler) which cools it from about 72° C. to about 16° C., thence to the strong-acid cistern t , whence it is taken for use as required.

It will be easily understood that the two towers effect an economy by considerably reducing the necessary amount of the most costly raw material, sodium nitrate, and that the Glover tower saves a considerable amount of coal by concentrating the acid and thus supplying steam to the chambers

by utilizing the heat from the pyrite burners. Moreover, by cooling, and, consequently, contracting the volume of the gases, it makes the existing chamber capacity so much more effective. The acid is further concentrated by evaporation in either glass or platinum vessels until a specific gravity of about 1.83 is reached, when it is brought into commerce as *concentrated sulphuric acid*.

34. A process that has been introduced successfully in the last few years is the *catalytic*, or *contact*, *process*. It depends on the fact that oxygen in the presence of platinized asbestos converts sulphur dioxide into sulphur trioxide; this with water gives sulphuric acid. The difficulties attending this process are very great; but they have been entirely overcome, and more than one factory is using this process for the manufacture of both sulphuric acid and sulphur trioxide from air and sulphur dioxide, without the use of oxides of nitrogen.

In this process one of four contact masses may be used, namely, (1) asbestos, clay, pumice, or other porous material coated with platinum; (2) crusts formed of an earthy or alkaline water-soluble salt coated with platinum; (3) porous or fibrous materials such as in (1) coated with copper sulphate; (4) ferric oxide (roasted pyrites). The second mass has a great advantage over the others, due to its activity on account of the fine division of the platinum and the relatively small quantity of platinum required, .1 per cent. and less of platinum being very efficacious, both because of its fine division and because the base used also possesses catalytic activity. It can also be readily regenerated and the platinum can be easily and completely recovered.

35. Diagram of Contact Process.—In Fig. 8 is shown a diagram of the apparatus used in a sulphuric-acid plant employing the contact process. The course of the various materials and products is indicated by the arrows. A is a bench of pyrites burners. The burner gas passes through the flue a_1 to the first cleaning tower B . Weak sulphuric acid is constantly flowing down this tower, becoming concentrated by the hot burner gas and absorption of the sulphur trioxide contained in the burner gas, and finally flows out at the bottom into the cooler C . From the cooler C , the strong acid passes to

the tank *D* and is delivered by the pump *D*₁ to the storage tank *T*, or to the tank *F* over the second cleaning tower *E*. A constant stream of strong sulphuric acid from the tank *F* is kept flowing down this tower. In this tower, the burner gas coming from the top of *B* is further cleaned and is then dried in the tower *I*; the circulation of the gases through the train of apparatus is maintained by the fan *J*. Before entering the contact ovens, the mixed gases are reheated to the proper temperature for the combination of the sulphur dioxide and oxygen in the reheater *K* and then are converted into trioxide in the contact oven *L*.

The sulphur trioxide now passes through the absorption cylinders *M*₁, *M*₂, *M*₃, *M*₄. These are connected in such a way that the gas passes from end to end, meeting the weak acid flowing in the opposite direction. Both the gas and the acid in *M*₁ are richest in sulphur trioxide, while in *M*₄ the gas and acid are weak. The strong acid coming from *M*₁ is ready for the market; it is collected in the tank *Q*, and delivered to the storage tank *R* by the pump *Q*₁. In order to recover the small amount of unabsorbed sulphur trioxide in the gases coming from *M*₄ these gases are passed through the tower *N*, which is supplied with weak acid from the tank *P*, which absorbs the last traces of the trioxide. The nitrogen and oxygen remaining pass into the air through the pipe *o*. From the tank *R* the acid is loaded into a tank car *S* for shipment.

36. Properties.—Sulphuric acid is a dense, colorless acid of oily consistency, having a specific gravity of 1.8372 at 15° C. It boils at about 338° C., and solidifies when cooled to a low temperature, the crystals thus formed having the composition H_2SO_4 , and melting again at 10.8° C. It may be distilled, but then undergoes a partial decomposition, the product containing but 98.7 per cent. of acid. It possesses an exceedingly strong attraction for water, combining with it with the evolution of great heat; it attracts moisture from the air, and from its avidity to absorb water is largely used in the laboratory as a drying agent for gases, the gas to be dried being caused to bubble through it. Sulphuric acid also attracts

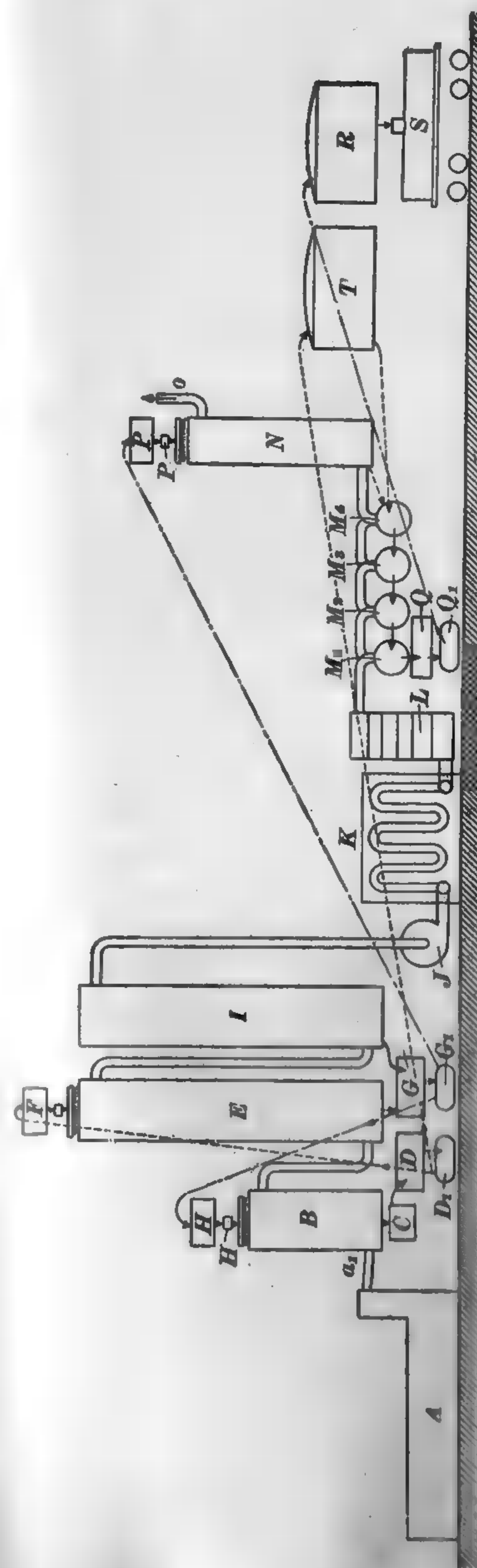


FIG. 8

most organic substances, removing the water from them, and thus completely charring or blackening them. When bodies have an excess of carbon that element is liberated. This property of sulphuric acid is turned into account in the manufacture of shoe blacking, in which treacle and sulphuric acid are employed.

EXPERIMENT.—Prepare a saturated solution of sugar and water; pour about 5 cubic centimeters of it into a beaker, and add all at once 10 cubic centimeters of sulphuric acid; the mixture suddenly froths up with great heat, a blackened and charred mass remaining.

When sulphuric acid and water are mixed, compounds are formed that have generally been considered the hydrates $H_2SO_4 \cdot H_2O$, and $H_2SO_4 \cdot 2H_2O$. Recent investigations, however, have made it appear that these compounds are more likely $SO(OH)_4$ and $S(OH)_6$. This latter would be normal sulphuric acid, and theoretically the other sulphuric acids would be derived from it by the loss of water, as in the case of the acids of iodine.

Even when largely diluted, sulphuric acid corrodes textile fabrics very rapidly, and though the acid is too dilute to appear to injure them at first, it will be found that the water evaporates by degrees, leaving the acid in a more concentrated state, and the fiber of the fabric is then perfectly rotten.

Sulphuric acid, being a dibasic acid, forms two well-marked series of salts; one is normal, but the other, still containing half the hydrogen, is acid. At a white heat, the acid is decomposed into water, sulphur dioxide, and oxygen.

37. Sulphuric acid is used directly or indirectly in hundreds of industries. It is used in the manufacture of all other mineral acids and of many organic acids. Enormous quantities are used in the manufacture of artificial fertilizers, alum, nitroglycerine, glucose, phosphorus, and dyes. It also finds a demand in such industries as dyeing, bleaching, electroplating, and refining. It is essential in one process for the manufacture of sodium carbonate, from which, in turn, are made soap and glass.

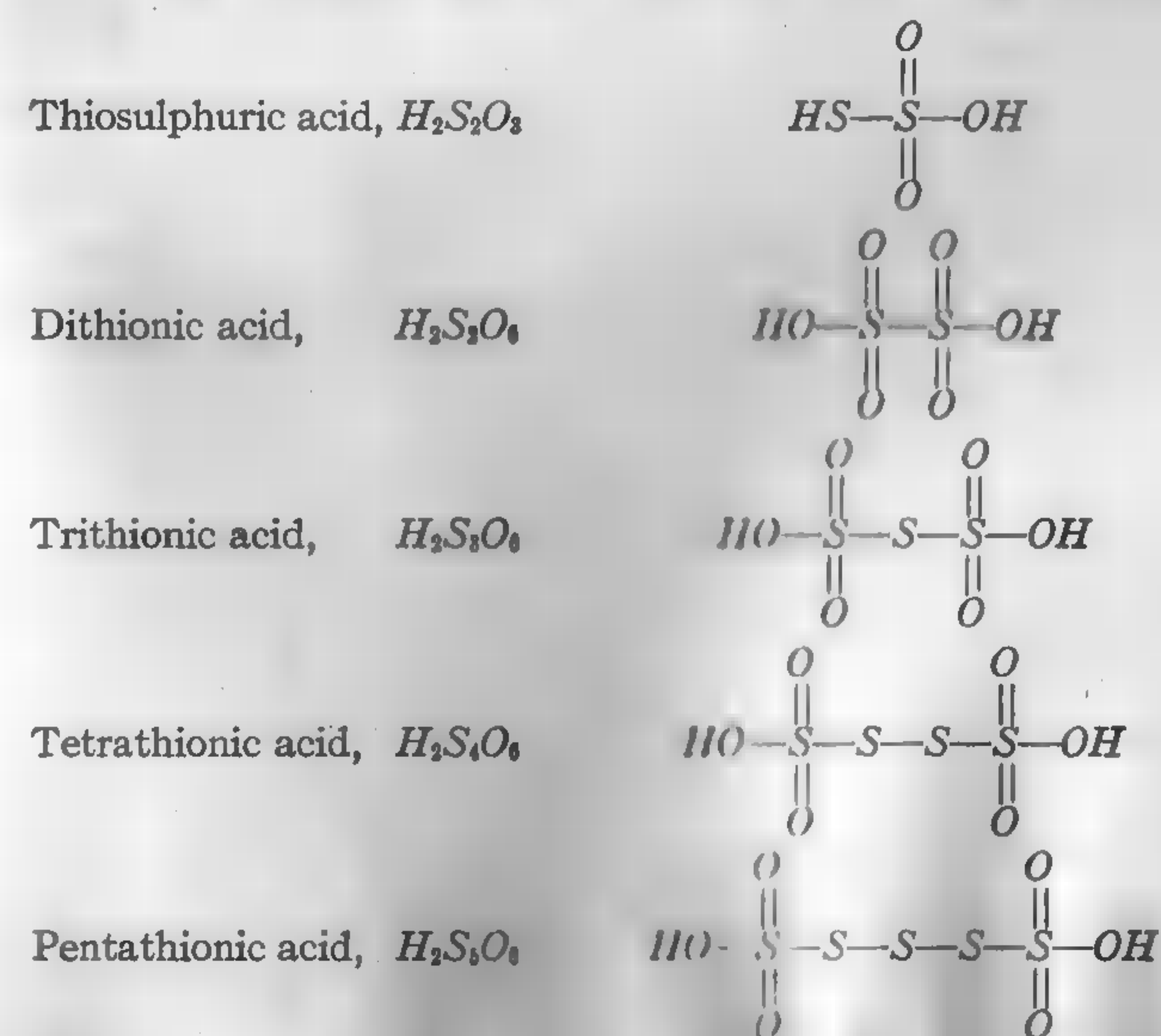
38. Pyrosulphuric, disulphuric, or Nordhausen sulphuric acid, $H_2S_2O_7$, is another kind of sulphuric acid met with in commerce. It may be regarded as a compound of a molecule of ordinary sulphuric acid with a molecule of sulphur trioxide:



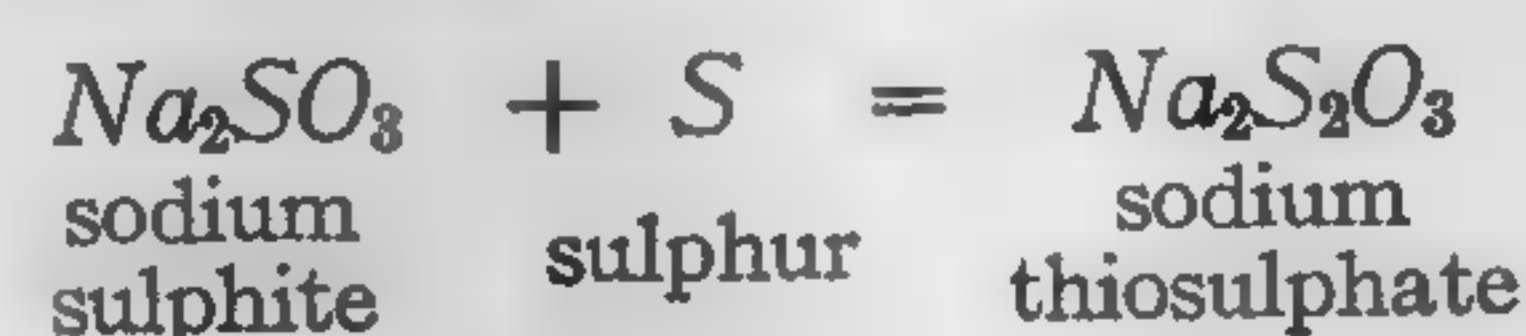
It is prepared by the distillation of partly dried ferrous sulphate in earthen retorts; it is named after a town in the province of Saxony, where it is manufactured on a large scale, and is used largely for dissolving indigo, with which the celebrated Saxony blues are made. It is a heavy, oily liquid of specific gravity 1.9. It is usually more or less dark colored, and hisses like a hot iron when dropped into water; it fumes strongly when exposed to air, and is consequently very often called *fuming sulphuric acid*. It is now manufactured on a large scale by conducting sulphur trioxide, made by passing sulphur dioxide and oxygen over platinized asbestos at a high temperature, through ordinary sulphuric acid. It is sometimes called solid sulphuric acid, because it solidifies when cooled, forming crystals that melt at $35^\circ C$.

39. Tests.—The test for free sulphuric acid is the characteristic charring it causes. Paper moistened in natural water containing sulphuric acid will be completely charred when dried at $100^\circ C$. Sulphuric acid and sulphates in a soluble form give a dense white precipitate with solution of barium chloride, insoluble in acids. If the sulphate is insoluble in water, it may be recognized by being fused with sodium carbonate, thus converting it into sodium sulphate, which is soluble in water, and may be tested as stated. Or, which is sometimes preferable, the suspected sulphate may be heated for some time with pulverized charcoal and sodium carbonate; it will thus be reduced to sodium sulphide, which, on treatment with a drop of acid, will evolve the well-known odor of hydrogen sulphide; or, placed on a piece of silver and moistened, will produce a black stain.

40. Thionic Series.—Besides the acids mentioned, which, with the exception of pyrosulphuric acid, contain but 1 atom of sulphur, there is a series of others that contains more than 1 atom (with different valences) of sulphur. This group is commonly known as the thionic series, derived from a Greek word meaning sulphur, and includes the following substances:



41. Thiosulphuric Acid, $H_2S_2O_3$.—Thiosulphates are prepared either by adding sulphur to a sulphite or by partial oxidation of a sulphide. By the first method:



Sodium thiosulphate, commonly but erroneously called sodium hyposulphite, is extensively manufactured for use in photography to fix plates and prints by dissolving the unaltered portion of the sensitive film of silver chloride, bromide, or iodide. It is also used in the chlorine bleaching process.

42. Summary.—Sulphur trioxide is a non-acid body produced by the union of sulphur dioxide with oxygen; the two combine when passed through platinized asbestos. It has no action on litmus, but has a great affinity for water, with which it produces sulphuric acid.

Sulphuric acid is a compound of great importance; it is formed by the oxidation of sulphurous acid, either by the atmosphere, or some oxidizing agent such as nitric acid, etc.

Sulphuric acid is manufactured by the reactions occurring between sulphur dioxide, oxygen, nitrogen trioxide, and also by the contact process and steam. The dilute acid is concentrated by evaporation. Nordhausen sulphuric acid is prepared by heating ferrous sulphate. Sulphuric acid is a colorless, odorless liquid, having a great attraction for water. Being a dibasic acid, it forms two series of salts called sulphates.

SULPHUR AND CHLORINE

43. Three compounds of sulphur and chlorine, *sulphur monochloride*, S_2Cl_2 , *sulphur dichloride*, SCl_2 , *sulphur tetrachloride*, SCl_4 , are formed by the direct union of their constituents. The first is formed when the sulphur is present in excess, the last when the chlorine is most abundant.

Sulphur monochloride, S_2Cl_2 , the most stable of the chlorides of sulphur, is an active, reddish-yellow liquid, specific gravity 1.087, possessing a peculiar, penetrating, disagreeable odor,

fuming strongly in the air, and boiling at $138^\circ C$. It is decomposed by metals, liberating sulphur and forming the chloride of the metal. Sulphur readily dissolves in the monochloride, forming a thick syrupy liquid containing 66 per cent. of sulphur.

Sulphur dichloride, SCl_2 , is prepared by passing chlorine to saturation into sulphur monochloride cooled by a mixture of ice and salt, and expelling the excess of chlorine by a stream of carbon dioxide. The compound thus obtained is a dark-red liquid boiling at $64^\circ C$., and having a specific gravity of 1.62. It decomposes even at ordinary temperatures into the monochloride and chlorine.

Sulphur tetrachloride, SCl_4 , is prepared by saturating sulphur monochloride with chlorine at a temperature of $-22^\circ C$. It is a yellowish-brown mobile liquid which only exists at temperatures below $0^\circ C$. When removed from a freezing mixture it immediately begins to dissociate with the evolution of chlorine. The tetrachloride exists not only in the free state, but also in combination with certain metallic chlorides, as $SnCl_4(SCl_4)_2$ with stannic chloride, and $SbCl_5(SCl_4)_3$ with antimonious chloride.

In addition to these, a number of compounds of sulphur with chlorine and oxygen are known that appear to be derivatives of sulphuric acid. For instance, the compound *sulphuryl chloride*, $\begin{array}{c} Cl \\ \diagup \\ S \\ \diagdown \\ Cl \end{array} \begin{array}{c} O \\ \diagup \\ \\ \diagdown \\ O \end{array}$ appears to be derived from $\begin{array}{c} HO \\ \diagup \\ S \\ \diagdown \\ HO \end{array} \begin{array}{c} O \\ \diagup \\ \\ \diagdown \\ O \end{array}$ by replacing each of the hydroxyl groups with an atom of chlorine.

SELENIUM

Symbol Se. Atomic weight 79.2. Molecular weight 158.4 (at $1,200^\circ C$). Density 78.6. Valence II, IV, and VI.

44. History.—The rare element selenium, was discovered by Berzelius in the year 1817. The name is derived from the Greek word *moon*, because of its resemblance to the element tellurium (the earth). It is also closely related to sulphur in its physical characteristics and its chemical relations to other bodies. Although selenium is somewhat widely dis-

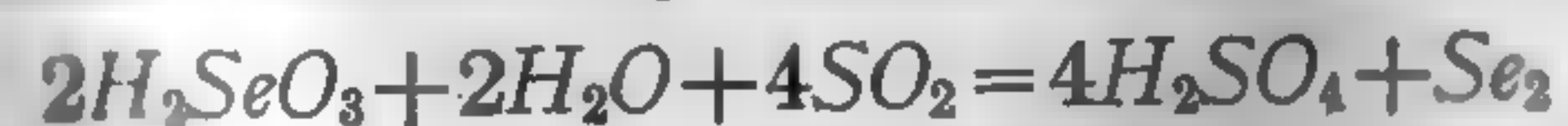
tributed it occurs only in small quantities. It occurs together with sulphur in Hawaii and in combination with minerals in Sweden, Argentine Republic, the Hartz Mountains, and in Mexico. It also occurs in small quantities with some sulphides of iron, copper, and zinc, but never native. Some iron pyrites contain selenium, and when these are roasted in the preparation of sulphuric acid, selenium settles out in chimney dust. It also occurs with tellurium in the flue dust obtained from some ores of gold and silver.

45. Preparation.—Selenium is prepared from the red deposit found in the flue dust of sulphuric-acid works by washing the scale with water and digesting with potassium-cyanide solution at 80° C. until the red color entirely disappears. It is then filtered and the filtrate treated with hydrochloric acid, which precipitates the selenium. This product is purified by oxidation to the oxide and is then sublimed and reduced to the metal by means of sulphur dioxide.

In some places the deposit from the flues is mixed to a thin paste with equal parts of sulphuric acid and water, and then the red color is destroyed by boiling with potassium chlorate or nitric acid. The solution is diluted with water, filtered, and heated with one-fourth its bulk of hydrochloric acid until about three-fourths of the liquid has evaporated, thus reducing selenic acid to selenious with the evolution of chlorine, thus:



The solution is now saturated with sulphur dioxide, which precipitates the selenium in fine, red flakes. This selenium is then separated from the lead and other metals it contains by sublimation or by fusion with potassium nitrate and sodium carbonate. The fusion is then dissolved in hydrochloric acid and the selenium reduced by means of sulphur dioxide, thus:



46. Properties.—Like sulphur, selenium exists in various allotropic modifications, three of which are known; namely, amorphous, crystalline, and metallic selenium. The first two are soluble in carbon disulphide, but the latter is not.

The amorphous modification is obtained as a brick-red powder when selenious acid is reduced in the cold by sulphur dioxide. It is also obtained when iron, zinc, or stannous chloride are used for the reduction, and also by the electrolysis of the acid. It has a specific gravity of 4.26 and is soluble in carbon disulphide. When a solution of amorphous selenium in carbon disulphide is poured into a large volume of ether it separates in a colloidal form, soluble in water, forming a red fluorescent solution that may be boiled without change. If the solution of amorphous selenium is heated to 217° C. and then rapidly cooled, vitreous selenium is formed. This solidifies as a brownish-black translucent mass and is very brittle.

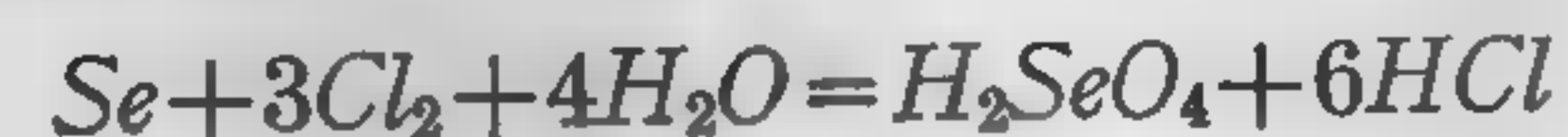
The crystalline modification is obtained when amorphous selenium is heated to 100° C. Its temperature suddenly rises to 217° C. in the act of crystallization. It is a dark-gray crystalline mass, crystallizing in prismatic crystals. It has a specific gravity of 4.5, and is soluble in carbon disulphide.

Metallic selenium is obtained by gradually heating the amorphous modification or by cooling melted amorphous selenium quickly to 210° C. and keeping the mass at this temperature for some time. It has a specific gravity of 4.8, is insoluble in carbon disulphide, melts at 217° C., boils at 660° C., and sublimates in black hexagonal crystals. It conducts electricity, and exposure to light increases its conductivity. Selenium burns in the air with a bright-blue flame emitting an odor of rotten horseradish.

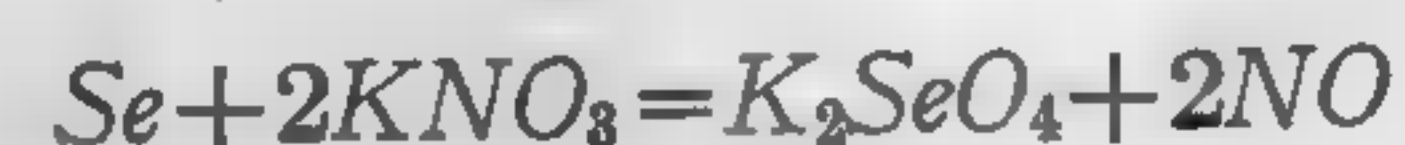
COMPOUNDS OF SELENIUM

47. Selenium dioxide, SeO_2 , is the oxide of selenium known with certainty to exist in the free state. Berzelius states that the peculiar odor given off by selenium when burned in the air is due to the formation of a lower oxide, but this oxide has never been isolated. The dioxide is obtained when selenium is strongly heated in a stream of oxygen, in the form of long white needles, which sublime without fusion at 320° C. It is readily soluble in boiling water, forming *selenious acid*, $SeO(OH)_2$.

48. **Selenic acid**, H_2SeO_4 , is prepared by the action of chlorine on selenium in the presence of water, thus:



Selenious acid and the selenites are converted in selenic acid and selenates in the same manner. By fusing selenium with potassium nitrate, the potassium salt of selenic acid is obtained, thus:



When subjected to concentration until a specific gravity of 2.6 is obtained, selenic acid becomes a colorless, very acid, oily liquid miscible with water in all proportions, with the evolution of heat. The hot acid dissolves gold and copper. Iron, zinc, and other metals dissolve in it, forming selenates with the evolution of hydrogen. Concentrated hydrochloric acid, when boiled with selenic acid, decomposes it with the formation of selenious acid and chlorine. This mixture will dissolve gold and platinum, owing to the chlorine set free. Sulphur dioxide and hydrogen sulphide do not reduce selenic acid, in which respect this acid differs from selenious acid.

Evaporated in a vacuum at $180^\circ C.$ and then cooled, selenic acid crystallizes in long, hexagonal prisms of the pure acid. These melt at $58^\circ C.$, have a specific gravity of 2.95, and combine readily with water, forming a monohydrate melting at $25^\circ C.$

49. **Hydrogen selenide**, H_2Se , also known as *hydro-selenic acid*, is prepared by treating iron selenide with hydrochloric acid. It is also formed by heating vapor of selenium with hydrogen from $250^\circ C.$ to $600^\circ C.$ It is a colorless gas possessing an odor which at first resembles hydrogen sulphide but later becomes more offensive; it is inflammable, and is very poisonous. Exposed to light, hydrogen selenide decomposes into its elements. It can be condensed to a liquid solidifying at $-64^\circ C.$, boiling at $-42^\circ C.$, and having a specific gravity of 2.1. Hydrogen selenide is soluble in water, reddens blue litmus paper, and colors the skin a reddish brown. The aqueous solution, on exposure to the air, decomposes with

the separation of red selenium. It produces precipitates of the selenides of the heavy metals, as does hydrogen sulphide.

50. **Halogen Compounds of Selenium.**—Selenium forms the following compounds with the halogens: Tetrafluoride, SeF_4 ; tetrabromide, $SeBr_4$; hexafluoride, SeF_6 ; monoiodide, SeI_2 ; monochloride, Se_2Cl_2 ; tetraiodide, SeI_4 ; tetrachloride, $SeCl_4$; chlorobromides, $SeCl_3Br$, $SeClBr_3$; monobromide, Se_2Br_2 . The *tetrafluoride* is a colorless fuming liquid boiling at a little over $100^\circ C.$, and the *hexafluoride* is a white crystalline mass at $-78^\circ C.$, and soon becomes gaseous when the temperature is raised. The *monochloride* exists as a brown, oily liquid that cannot be distilled without decomposition. *Selenium tetrachloride* is a light-yellow solid, volatilizes readily, and sublimes in small crystals. The *monobromide* forms a black, almost opaque, liquid with a disagreeable odor. Acted on by bromine, it changes to the *tetrabromide*. This is an orange-yellow crystalline mass, is volatile, vaporizing between $75^\circ C.$ and $80^\circ C.$ with slight decomposition, recrystallizing in black six-sided scales. It has a peculiar disagreeable odor, and decomposes in moist air. The *mono-* and *tetra-iodides* are both crystalline. The former crystallizes in a black shining mass that melts at $70^\circ C.$, and the latter forms dark granular crystals that melt at $80^\circ C.$ to a brownish-black liquid. The *chlorobromides* both form orange-yellow crystalline substances.

TELLURIUM

Symbol *Te*. Atomic weight 127.5. Valence II, IV, and VI. Density 127.0. Specific gravity 6.24.

51. **History and Occurrence.**—Tellurium occurs in small quantities in a few places in Germany, Mexico, United States, Brazil, Bolivia, and Australia. It also occurs native. In 1798 Klaproth made an investigation of the tellurium ores and named the metal tellurium, from *tellus*, the earth. From exhaustive investigations of tellurium and its compounds it was decided that the substance itself was a metal. Its compounds, however, were found to resemble so closely those of

sulphur and selenium that it was placed in the sulphur group. It is usually found in combination with other metals, as with gold and silver in *sylvanite*, $(AgAu)Te_2$; with silver as *hessite*, Ag_2Te ; with bismuth as *tetradymite*, Bi_2Te_3 ; etc.

52. Preparation.—Pure tellurium is prepared from tetradymite (bismuth telluride), which is mixed with an equal quantity of pure sodium carbonate, the mixture made into a thick paste with oil, and heated strongly in a tightly closed crucible. The fusion is then leached with air-free water and the solution filtered. Air is passed through this filtered solution, which precipitates the tellurium in the form of a gray powder. This is further purified by distillation in a stream of hydrogen.

Occurring as it does in combination with gold and silver, it is found in the fume chambers of gold and silver smelters. This fume is digested with sodium carbonate and potassium cyanide and the solution decanted, the solution acidified with nitric acid, and the tellurium precipitated by hydrogen sulphide.

53. Crude tellurium is best purified by dissolving in aqua regia (nitro-hydrochloric acid). The excess of nitric acid is expelled by evaporation with an excess of hydrochloric acid. The concentrated liquid is then diluted to keep the tellurous acid in solution and to precipitate the lead chloride. The lead chloride is removed by filtering and the tellurium precipitated by sulphurous acid. The tellurium thus obtained is then distilled in a current of hydrogen.

54. Properties.—Tellurium is a silver-white, brittle, crystalline solid with a strong metallic luster and a specific gravity of 6.24. It conducts heat and electricity readily, and crystallizes in rhombohedrons. It melts at $452^\circ C.$, volatilizes at $1,300^\circ C.$, and can be distilled. Its vapor is greenish-yellow, resembling that of chlorine. When heated in the air it takes fire and burns with a blue flame tinged with green, evolving white fumes of tellurous oxide. In all its physical properties, tellurium closely resembles a metal, but, being so closely allied, chemically, to sulphur and selenium, it is justifiable to

regard it as a non-metal and consider it with these elements. Its binary compounds are known as *tellurides*. It forms two chlorides, $TeCl_2$ and $TeCl_4$, and two bromides having the same composition.

REVIEW OF SULPHUR GROUP

55. The same gradation of properties that has been noticed in the halogen group may be noticed between the closely allied elements sulphur, selenium, and tellurium, commonly known as the sulphur group. The sum of the atomic weights of sulphur and tellurium ($32.07 + 127.5$) is but slightly more than double that of selenium (79.2). All these elements form similar compounds with hydrogen, H_2S , H_2Se , and H_2Te , in which they are bivalent; and the last three form oxides in which their valence is 4 and 6; as SO_2 and SO_3 , SeO_2 , TeO_2 , and TeO_3 , to each of which there is a corresponding acid. While the general chemical activity of these elements decreases with the increase in atomic weight, the stability of the halogen compounds increases with the increase in atomic weight. OCl_2 is very unstable, SCl_2 and SCl_4 only exist at low temperatures, but $SeCl_4$, $TeCl_2$, and $TeCl_4$ even exist as gases.

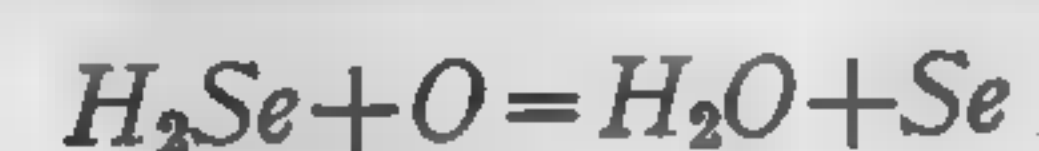
THERMOCHEMICAL RELATIONS

56. The thermochemical relations of the elements sulphur, selenium, and tellurium and their compounds largely explain their chemical behavior. When hydrogen and oxygen unite to form water, the equation is $H_2 + O = H_2O + 68,360 \text{ cal.}$ That is, 2 grams of hydrogen uniting with 15.88 grams of oxygen forming water gives off 68,360 calories. Part of this heat is used in converting the water formed into steam, so that the equation in the case of steam would be, $H_2 + O = H_2O (\text{steam}) + 57,200 \text{ cal.}$

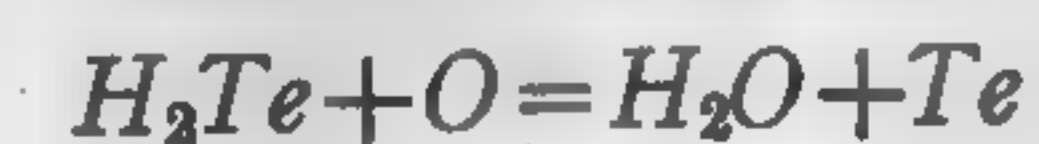
When hydrogen unites with solid sulphur to form hydrogen sulphide, 4,500 calories are developed, so that for hydrogen-sulphide gas the equation is $H_2 + S = H_2S + 4,500 \text{ cal.}$ When this gas is dissolved in a large quantity of water 4,700 more

calories are developed, so that the total heat of formation of hydrogen sulphide in dilute aqueous solution is 9,200 cal.

Hydrogen, selenide, and telluride are endothermic compounds, the equation for hydrogen selenide being $H_2 + Se = H_2Se - 5,400$ cal. They are, therefore, unstable compounds. When in aqueous solution, oxygen will replace these elements from H_2Se and H_2Te , forming water, thus:



and



INORGANIC CHEMISTRY

(PART 6)

FAMILY 5, GROUP B

GENERAL REMARKS

1. Family 5, Group B, contains the elements *nitrogen, phosphorus, arsenic, antimony, and bismuth*. The element nitrogen bears the same relation to the other members of this group that fluorine bears to the other members of Group B, Family 7, and that oxygen bears to the other members of Group B, Family 6. That is, the relationship between nitrogen and the other members of the group is not so close as is that existing between the other members of the group. Speaking broadly, it may be said that all the members of the group form compounds of similar character and composition. There is, however, a gradual gradation of properties from nitrogen to bismuth. While as a whole the members of this group are acid formers, this property is less marked as we pass toward the heavier elements. Thus, nitrogen forms strong acids; phosphorus and arsenic, less strong; antimony, almost as many basic as acid compounds; bismuth more basic than acid. The hydrogen compounds of these elements grow less stable from nitrogen to antimony, and bismuth will not form a compound with it. The hydrogen compounds are: NH_3 , PH_3 , AsH_3 , and SbH_3 . The first one, NH_3 , is strongly basic; the corresponding compound of phosphorus is weakly basic, while the hydrogen compounds of arsenic and antimony have no

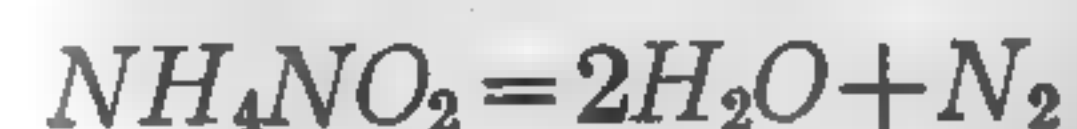
basic properties. Thus it is seen that in this group, as in the other groups that have been studied, there is a gradual gradation of properties from the light to the heavy elements.

NITROGEN

Symbol N. Atomic weight 14.01. Density 14.0. Valence I, III, V. Specific gravity .971. Molecular weight 28.02. 1 liter weighs 1.2507 grams.

2. History and Occurrence.—Nitrogen was discovered in 1772, by Rutherford, who showed that air, after it had been breathed by an animal and washed with lime water, contained a gas that would support neither respiration nor combustion. Scheele and Lavoisier soon afterwards found, independently of each other, that this substance constituted four-fifths of the air. Lavoisier gave it the name of *azote*, and Chaptal later proposed the name of *nitrogen*. It exists in the free state in the atmosphere, and in combination with oxygen and metals in certain native nitrates, besides being an essential constituent of many vegetable and animal substances.

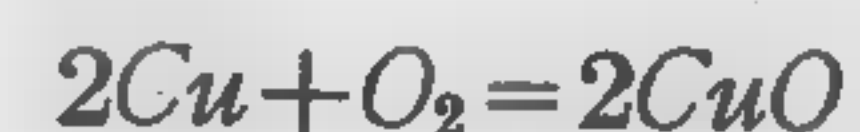
3. Preparation.—The easiest method of preparing nitrogen is by burning out of a given volume of air the oxygen that it contains, thus leaving the nitrogen. The nitrogen prepared in this way, however, is never entirely pure, being contaminated with gases from the helium group and small quantities of carbon dioxide and unburned oxygen. It may also be procured by purely chemical processes; as, for instance, by heating ammonium nitrite:



It is best prepared by this method by heating a solution of 1 part of sodium nitrite, 2 parts of ammonium-sulphate, and 1 part of potassium dichromate, the latter preventing the formation of nitric oxide. The gas is washed by passing it through dilute sulphuric acid.

EXPERIMENT.—Nitrogen may be obtained from air by burning out the oxygen by means of phosphorus. A small piece of phosphorus, carefully dried, is placed in a light receptacle floated on the surface of water by means of a piece of cork. The phosphorus is lighted and then quickly covered with a good-sized bell jar, as shown in Fig. 1. Dense white fumes that fill the jar are formed by the combustion; the oxygen is gradually consumed; and the water rises in the bell jar to take its place. After a short time these fumes disappear, and the nitrogen is left comparatively pure.

The oxygen may also be removed by the action of metallic copper. If an iron tube is filled with copper turnings, and made red hot in a furnace, the copper immediately combines with the oxygen of any air that may be passed through, leaving the nitrogen, thus:



Iron likewise removes the oxygen from air, especially if caused to oxidize more readily by the addition of some ammonium chloride.

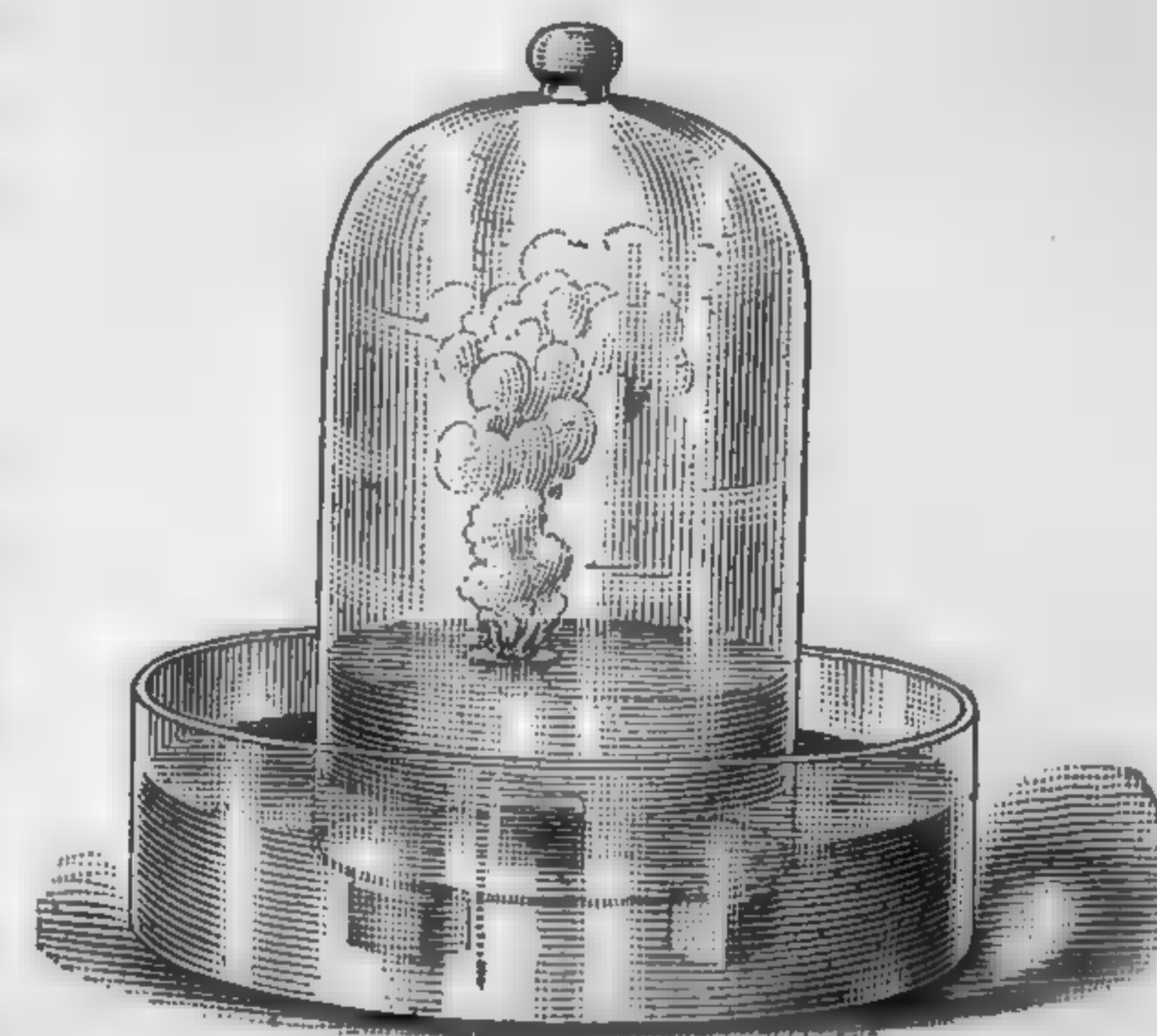
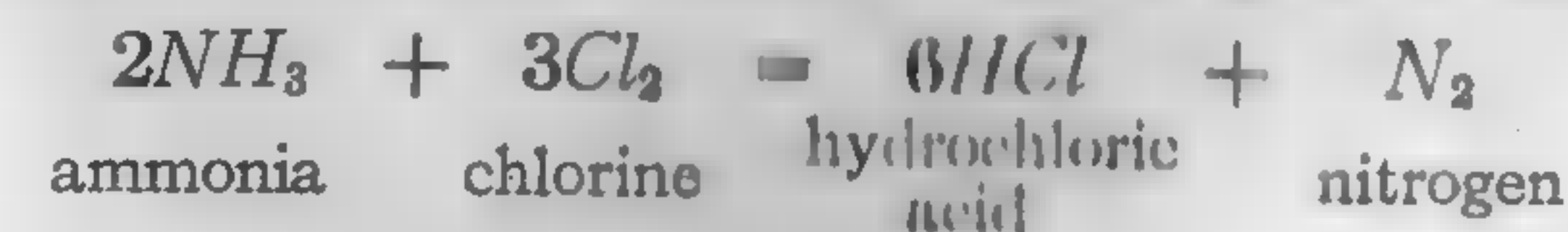
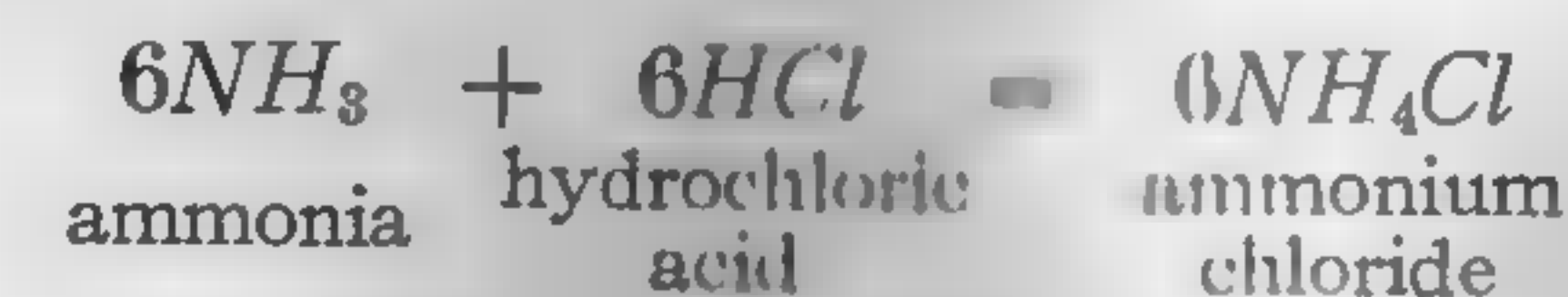


FIG. 1

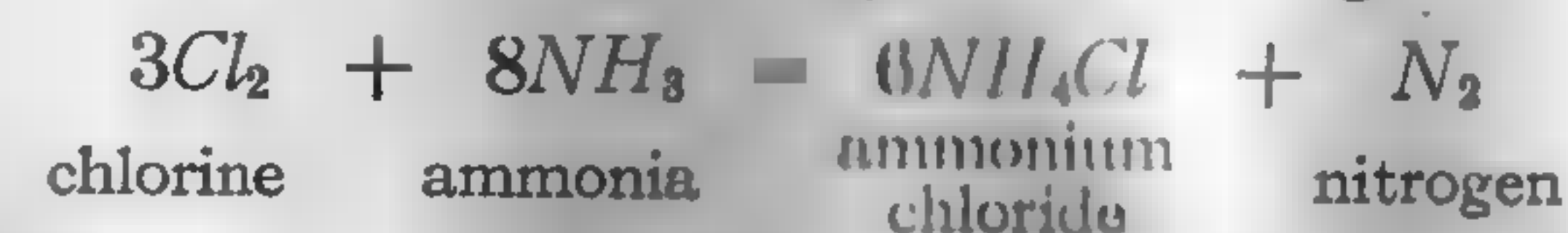
4. There are various other methods of preparing nitrogen, all of which are interesting from a theoretical point of view. For instance, the gas is evolved by passing chlorine into an excess of ammonia. The hydrogen and chlorine unite, and nitrogen is liberated:



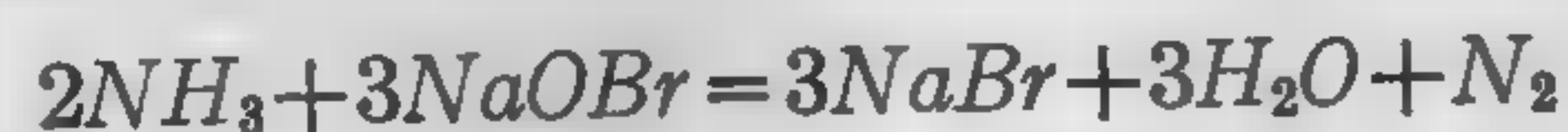
A secondary reaction goes on between the acid formed and the excess of ammonia, thus:



These two reactions may be expressed through one equation:



If a solution of ammonia or of an ammonium salt is treated with an alkaline solution of sodium hypobromite, nitrogen is evolved, thus:



This nitrogen is obtained in a perfectly pure condition by washing it through dilute sulphuric acid, and dilute caustic soda and then passing it over heated copper and copper oxide.

5. Properties.—Nitrogen is an odorless, colorless, and tasteless gas; it is somewhat lighter than air, and has a specific gravity of .971. It extinguishes burning bodies and is not combustible itself. Water dissolves only $\frac{1}{50}$ of its volume of nitrogen at 0°. Animals are quickly suffocated in an atmosphere of pure nitrogen, though the gas by itself does not exert any poisonous influence on the animal economy. It has been liquefied at temperatures below -146°C ., and under a pressure of 1 atmosphere this liquid boils at -195.5°C .

Liquid nitrogen is colorless, and when evaporated in a vacuum solidifies, forming a colorless, crystalline mass, which melts at -210.5°C ., and has a specific gravity at its boiling point of .81.

Nitrogen, in a free state, is a remarkably inert body, combining directly with only a very small number of elements, among which are magnesium, silicon, boron, and titanium, but its compounds are among the most energetic known. The corrosive nitric acid, the pungent ammonia, the explosive nitroglycerine, and even such an active poison as prussic acid, as well as numerous alkaloids, all contain more or less nitrogen.

6. Summary.—Nitrogen exists in a free state in the atmosphere, and is also found in nitrates and various organic bodies. It is prepared by the removal of oxygen from the air by the action of either phosphorus or copper, or by the decomposition of bodies containing nitrogen, as ammonium nitrite and ammonia. It is a colorless, tasteless, and odorless gas, neither inflammable nor a supporter of combustion; it is neutral to litmus paper; it may be liquefied; by great heat it may be made to combine with oxygen, forming acid compounds.

THE ATMOSPHERE

A gaseous mixture. Density 14.43. Specific gravity 1.

7. Occurrence.—The aerial envelope that surrounds the earth and is of vital importance to all beings that live and breathe in it, is called the **atmosphere**. Its existence is demonstrated whenever it is set in motion, as then we have *winds*, which, when sufficiently violent, produce well-known and striking physical effects.

8. Properties.—Careful experiments have shown that, among other properties of matter, the atmosphere possesses weight. Regnault has shown that air, which has been chosen as the standard of specific gravity for gases, is 14.43 times heavier than hydrogen. Torricelli showed, in 1643, that the pressure of the air on the earth's surface would sustain a column of mercury about 76 centimeters in height; and, as a column of mercury of this height, with an area of 1 square centimeter, weighs 1,033 grams, it follows that this number represents the atmospheric pressure on every square centimeter of the earth's surface.

9. Composition.—The atmosphere consists chiefly of a mixture of nitrogen with $\frac{1}{5}$ volume of oxygen. In addition to these two elements, there are also present varying quantities of aqueous vapor, carbon dioxide, ammonia, nitric acid, and traces of argon, neon, helium, krypton, and xenon. The average composition of the atmosphere is approximately shown in Table I.

TABLE I

Oxygen.....	20.61 parts
Nitrogen, argon, etc.....	77.95 parts
Carbon dioxide.....	.04 part
Aqueous vapor.....	1.40 parts
Nitric acid.....	Traces, according to the loca- tion—whether city, village, seashore, etc.
Ammonia.....	
Methane.....	
Hydrogen sulphide.....	
Sulphur dioxide, etc.....	

Although the proportion of oxygen in the air at a given spot may be diminished, and that of carbon dioxide increased

by processes of oxidation (such as respiration and combustion) taking place there, the operations of wind and diffusion so rapidly mix the altered air with the greater general mass of the atmosphere, that the variations in the composition of air in different places are very slight.

10. The composition of the atmosphere is generally expressed in terms of the quantity of oxygen and nitrogen contained in it, argon and nitrogen usually being classed as nitrogen. In determining these elements, care must be taken to exclude any errors due to the presence of carbon dioxide, ammonia, aqueous vapor, etc. The composition of the atmosphere is determined by means of the apparatus shown in Fig. 2. This apparatus was devised by Dumas and Boussingault.

The atmosphere is passed through the *U* tubes *A*, which are filled with potassium hydrate to remove any carbon dioxide, then through the *U* tubes *B* containing sulphuric acid, which removes the water and ammonia. The atmosphere is now passed through the tube *C*, which is filled with metallic copper and placed in a furnace so that it can be heated to redness: The globe *D* and the tube *C* are exhausted by means of an air pump, and are accurately weighed. The apparatus is connected, the tube *C* is heated to redness, the stop-cocks *E* and *E*₁ are opened to allow the air to pass slowly through the apparatus. The air in passing through the tube *C* has all the oxygen removed by its absorption by the heated copper, and only the nitrogen passes over in the globe *D*. After a quantity of air has passed through *C* the stop-cocks are closed and after cooling the globe and tube are weighed. The weight of the tube is the weight of the oxygen plus some nitrogen, and the weight of the globe represents a part of the nitrogen. The tube is exhausted, the nitrogen it contained being withdrawn and again weighed. The difference in these latter weights of the tube is added to the weight of nitrogen in the globe, and the difference between the first and last weights of the tube represent the oxygen in the air.

11. The *eudiometric* method for determining the composition of the air does not require as elaborate an apparatus



FIG. 2

as the foregoing method. The method is also less tedious and difficult and is accurate. The process depends on the combination of oxygen and hydrogen in the presence of a spark. Air and hydrogen are introduced into a eudiometer and an electric spark is passed through the mixture. The oxygen of the air unites with a certain quantity of the hydrogen, and on cooling the water vapor thus formed condenses, causing a contraction in the volume of the air in the eudiometer. One-third of this contraction is due to the oxygen in the air. Of course, all carbon dioxide, water, and ammonia must be absorbed from the air previous to making the analysis.

12. Air a Mixture.—The fact that air is a mixture and not a chemical compound may be proved in numerous ways. In the first place, the oxygen and nitrogen are not present in any simple multiple of their atomic weights, which is necessary in all chemical compounds. Air differs also greatly from all compounds of these two elements with which chemistry is acquainted. If a mixture is made of nitrogen and oxygen in the proportion in which they exist in air it will be found that no alteration of volume takes place, and that there is no increase of temperature; the mixture simply exhibits all the properties of ordinary atmospheric air.

The most conclusive evidence that these gases are mixed and not combined is that they may be separated by the action of water as a solvent. Oxygen is much more soluble than nitrogen, and if water that has been freed from gases by boiling is shaken with air and again boiled, the expelled gas is found, on analysis, to be much richer in oxygen than was the air, the oxygen amounting to about 34 per cent. of the dissolved gas.

13. Summary.—The atmosphere is a mixture, and not a compound, of oxygen and nitrogen, in which small quantities of other substances are also present.

14. Rare Elements in the Air.—Lord Rayleigh has shown that 1 liter of nitrogen prepared by removing the oxygen of air weighs 1.2572 grams, whereas a liter of nitrogen prepared chemically weighs 1.2505 grams. This would indicate that there is in the air some substance heavier than nitrogen

that remains with the nitrogen. This led Lord Rayleigh and W. Ramsey to carefully investigate the composition of the air, when they discovered that it contains at least five previously unknown substances, which are present in the following proportions:

Argon,	1 volume in	100 volumes of air
Neon,	$1\frac{1}{2}$ volumes in	100,000 volumes of air
Krypton,	1 volume in	20,000,000 volumes of air
Xenon,	1 volume in	170,000,000 volumes of air
Helium,	1 volume in	250,000 volumes of air

AMMONIA

Formula NH_3 . *Density* 8.517. *Molecular weight* 17.034.

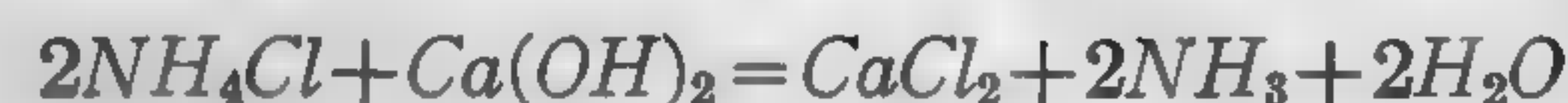
15. History.—Ammonia has been known for many centuries. The alchemist Raymond Lully mentions it in his manuscript in the 13th century, and Basil Valentine used it experimentally in the 15th century. Priestly, in 1774, first obtained it as a gas, and in 1777 Scheele analyzed it and showed it to contain nitrogen.

16. Occurrence.—Ammonia exists, in the free state, in small quantities in the air and in rain water. It is generally a post-mortem product, as dead animal and vegetable matter yields it in putrefaction. The urine and excrement of animals contain refuse nitrogenous matter that, on being exposed to the air, is changed into ammonia, and in this way causes these substances to be such valuable fertilizers, as most plants are incapable of assimilating nitrogen in a free state, but are able to do so when that element is presented to them as ammonia.

The compounds of ammonia are found in beds of guano (the excrement of sea fowl) on certain ocean islands, etc.; the most important of these compounds, ammonium chloride, formerly called sal ammoniac, was first obtained from Egypt. The name ammonia is said to be derived from that of Jupiter Ammon, owing to the circumstance that near a temple dedicated to this god the Arabs extracted one of the compounds

of ammonia from the dung of camels. Quills, horn, hair, etc. heated in a closed vessel evolve a number of gases, among which ammonia is always present. Coal (fossilized plants) contains about 2 per cent. of nitrogen, and in its destructive distillation for the manufacture of gas, ammonium compounds are always obtained.

17. Preparation.—Ammonia cannot be produced by the direct union of its constituents, but it may be prepared from any of the ammoniacal salts by heating with a stronger base, such as lime or soda. Of these, lime is mostly chosen on account of its cheapness. If, for instance, ammonium chloride and slaked lime are heated together, the following reaction occurs:



In order to thoroughly decompose the ammonium chloride, about 2 parts of lime are used to 1 part of the ammonium chloride.

EXPERIMENT 1.—Place a mixture of 2 parts of dry, powdered lime, and 1 part of ammonium chloride in a dry Florence flask fitted with a stopper and a dry delivery tube, as shown in Fig. 3. Apply a gentle heat to the flask and collect the evolved gas by upward displacement in a dry bottle. Owing to the solubility of ammonia in water it cannot be collected over water. When the bottle is full, which can be told by the turning blue of a piece of red litmus paper held just inside the mouth of the bottle, withdraw the delivery tube, lift the bottle from the ring that supports it, and place a cover over the mouth of the bottle.

EXPERIMENT 2.—Place 15 cubic centimeters of dilute hydrochloric acid in a beaker, connect the delivery tube by means of a rubber tubing with another glass tube dipping into the hydrochloric acid. Continue the evolution of ammonia until a piece of blue litmus paper dipped into the solution in the beaker is no longer reddened. Evaporate to dryness and compare the residue to the original ammonium chloride.

The most convenient method of obtaining gaseous ammonia in the laboratory is to gently heat strong ammonium hydroxide in a retort such as shown in Fig. 4.

18. Properties.—Ammonia is a colorless gas that is readily distinguished by its characteristic odor and its powerful alkaline action on red litmus paper. It is considerably lighter

than air, its specific gravity being .589. Subjected to a pressure of $6\frac{1}{2}$ atmospheres at 10°C . or to a cold of -40°C ., it condenses to a colorless liquid of specific gravity .6362, which freezes at -75°C . and boils at -35.7°C . It is soluble in water to an extraordinary degree, 1 volume of water at 0°C . absorbing 1,149 volumes of ammonia gas, forming the so-called *aqua*

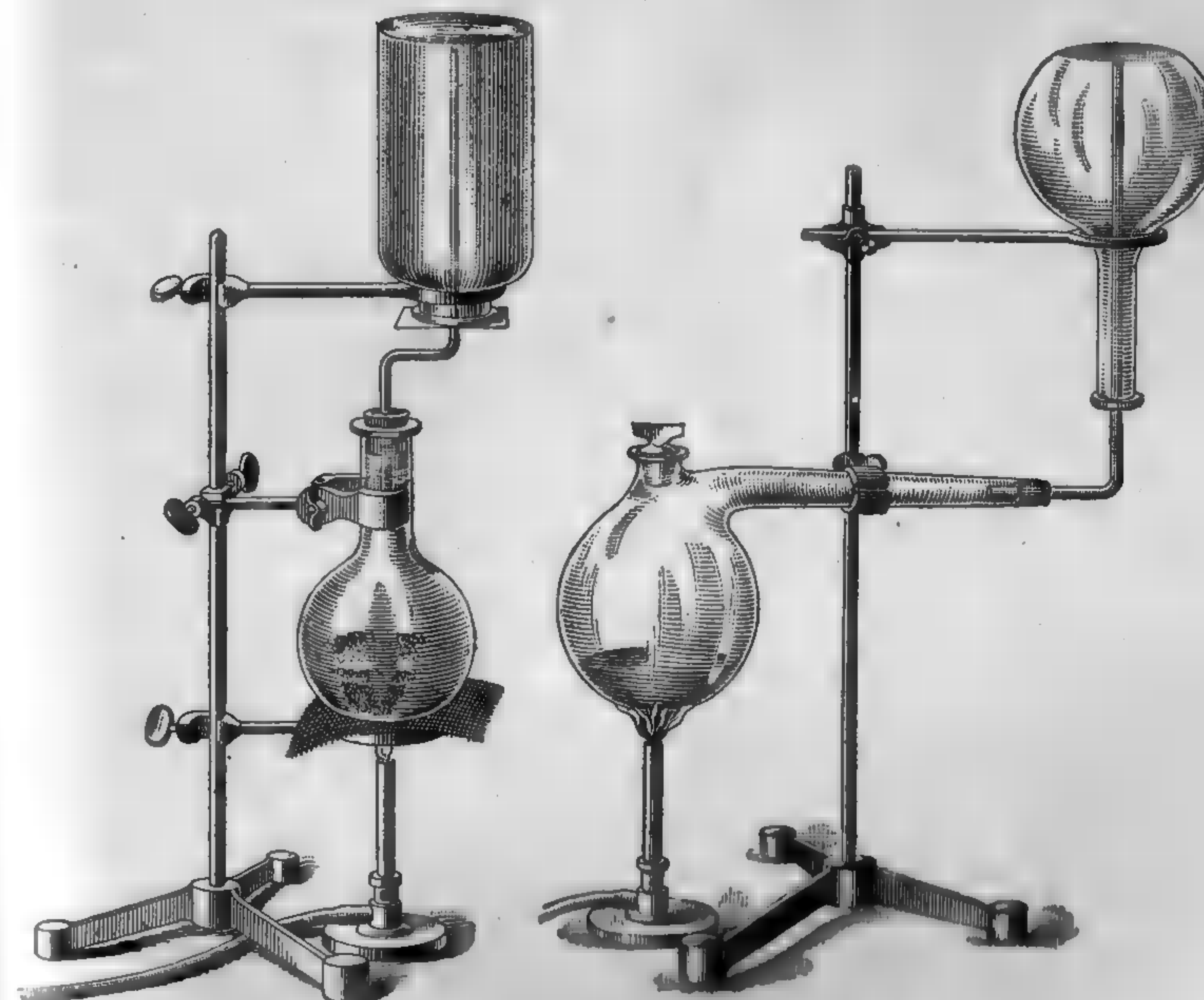
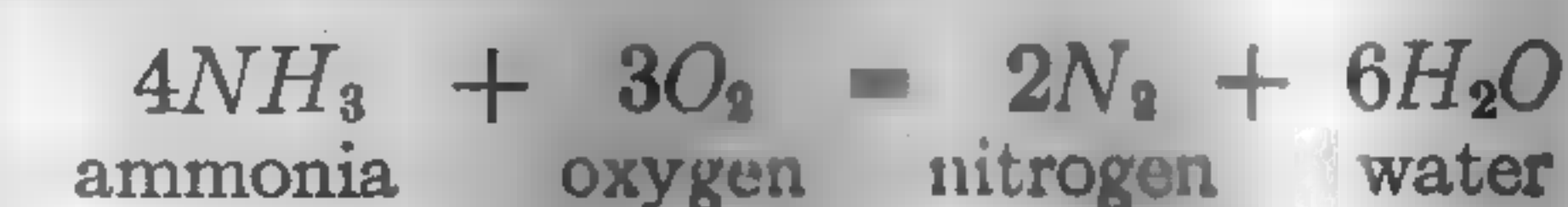


FIG. 3

FIG. 4

ammonia. At 15°C ., 1 volume of water absorbs 783 volumes of the gas.

Chemically, ammonia gas has a strong but transient alkaline action on vegetable colors, from which quality the name *volatile alkali*, sometimes given to ammonia, originates. Ammonia is a non-supporter of combustion and is not readily combustible in the air, but in oxygen it ignites readily and burns with a pale yellowish flame, water being produced and nitrogen set free, according to the equation:



The liquid ammonia of commerce is a solution of gaseous ammonia in water. It is prepared by passing the gas into a flask of water kept cool by being placed in a vessel of cold water.

The commercial liquid ammonia is usually prepared directly from the ammoniacal liquor obtained from gasworks instead of using ammonium chloride. The liquor is heated with lime water in a still and the gas passed through coolers. It is then washed by passing it through lime water and charcoal, after which it is absorbed in water.

19. The percentage of ammonia in solution is determined by means of its specific gravity, the higher the specific gravity, the lower the percentage of ammonia in the solution. Table II

TABLE II
STRENGTH OF AMMONIA SOLUTIONS

Specific Gravity	Percentage NH_3	Specific Gravity	Percentage NH_3
.8844	36	.9251	20
.8864	35	.9414	15
.8976	30	.9593	10
.9106	25	.9790	5

gives the percentage, according to Carius, of ammonia in solutions of different specific gravity.

20. **Carré's Freezing Apparatus.**—When liquid ammonia is allowed to evaporate it absorbs a large amount of heat. This property has led to its use for the artificial production of ice. In Fig. 5 is shown a freezing apparatus invented by M. Carré which does not require a force pump. The iron boiler *A* contains a concentrated solution of ammonia in water. This is heated gradually and the ammonia gas is driven over into the double-walled receiver *B*, which is cooled in water, when the gas condenses. After the greater part of the gas has been expelled from *A* the apparatus is reversed. The boiler *A* is cooled with water, and the liquid to be frozen is placed in a

cylinder *C* that fits into *B*. The liquid ammonia in *B* rapidly evaporates and is reabsorbed by the water in *A*. This evaporation is accompanied by an absorption of heat, thus cooling *B* to below the freezing point. For ice making and refrigeration on a large scale, ammonia is condensed by compression in metal tubes cooled by water. The liquid ammonia is then circulated through pipes in contact with brine or the air space to be cooled. It evaporates in these pipes, producing a rather low temperature, and the gas passes back to the pump to be compressed again.

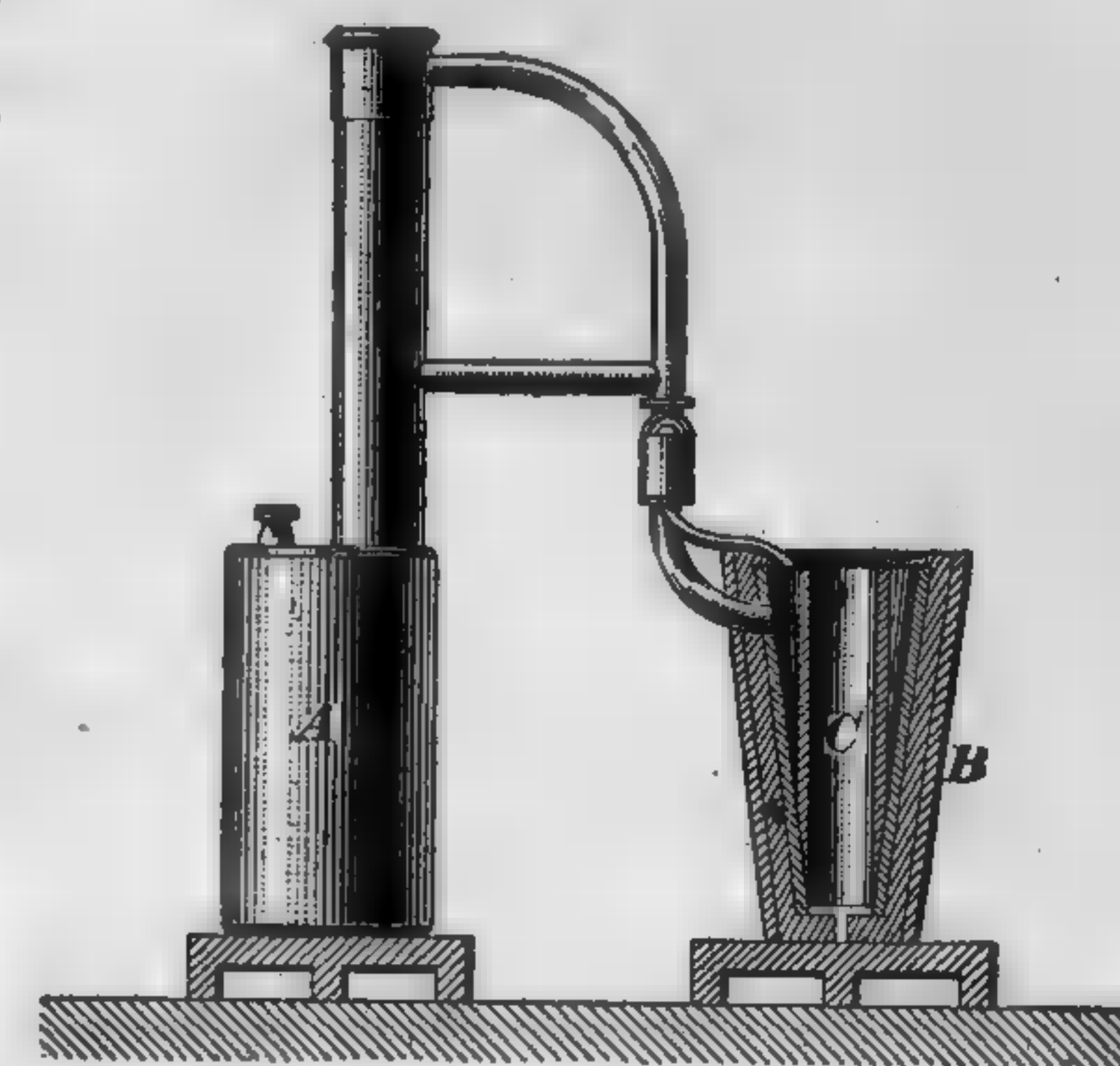
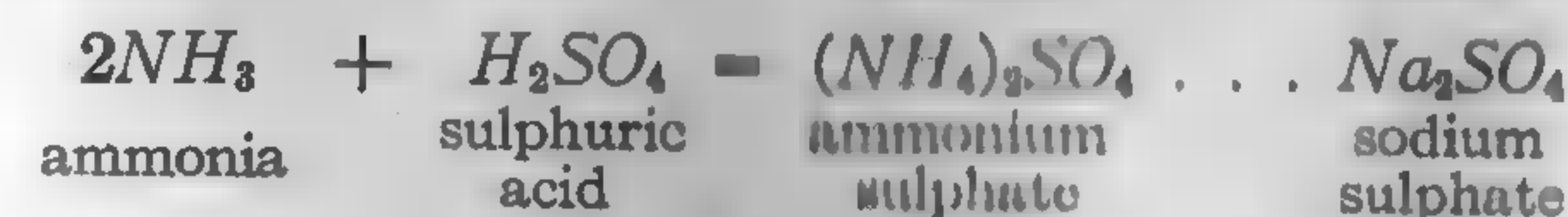
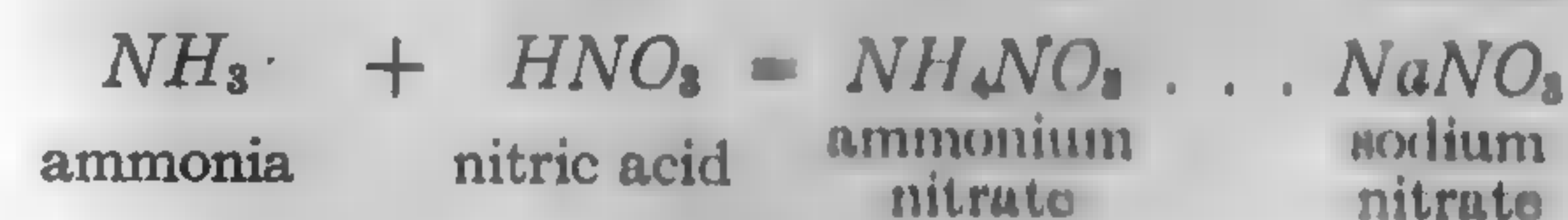
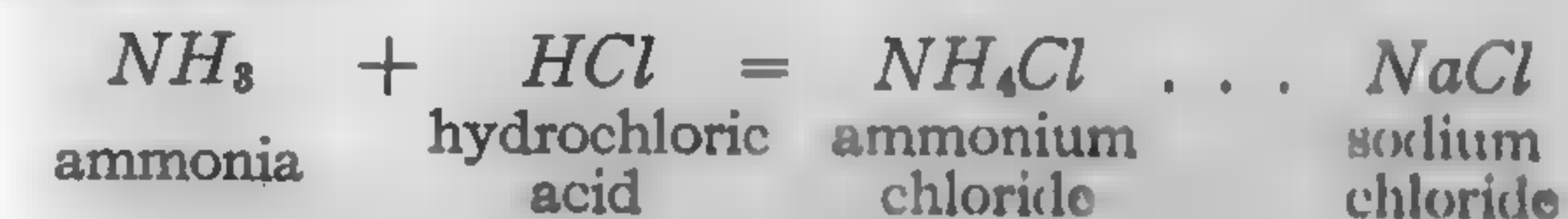


FIG. 5

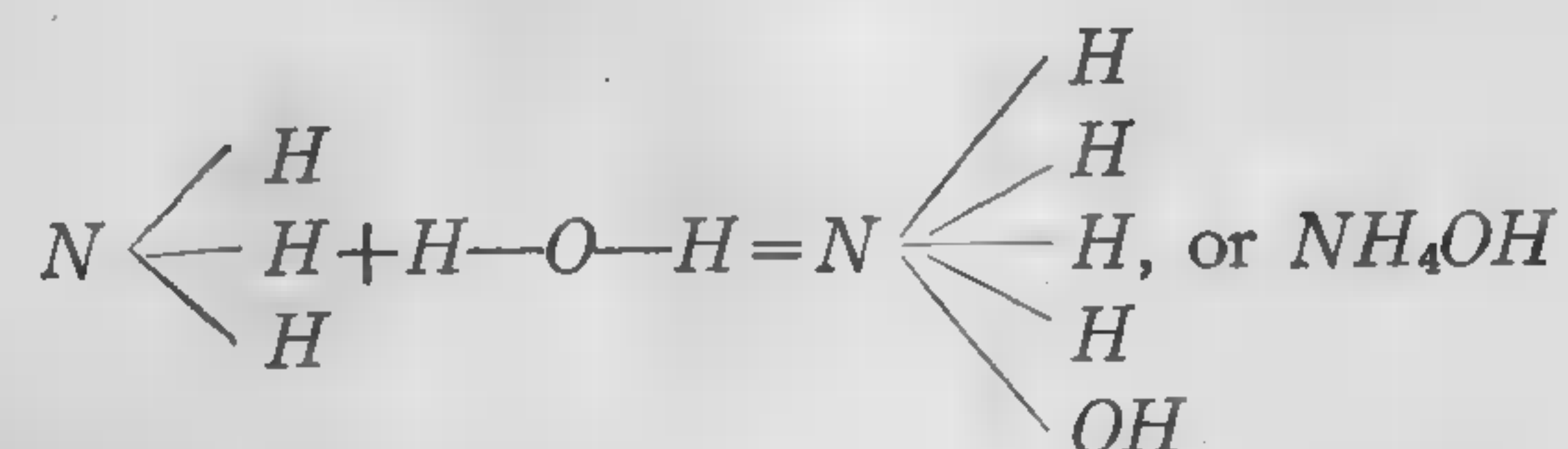
21. Experiment 1, Art. 17, showed that ammonia restores the blue color to litmus paper reddened by an acid. It neutralizes the strongest acids and forms a well-marked and most important series of salts. The composition of some of these is shown by the following equations:



The salts of sodium are given in the last column for the sake of comparison. It will be noticed that the group NH_4 and sodium occupy corresponding places. Furthermore, this group may be expelled from one chemical compound and caused to enter another without decomposition.

The group NH_4 is one of the best and most striking examples of a *compound radical*; it behaves in so many compounds

as if it were an element that it has received the name *ammonium*. It cannot, however, be isolated, for it immediately decomposes into ammonia and free hydrogen. Ammonium chloride is written NH_4Cl . As previously stated, it is thought the valence of the nitrogen changes from 3 to 5 when ammonia is dissolved in water, and that ammonium hydrate is formed thus:



This, again, is analogous in composition to sodium hydrate, $NaOH$. Ammonium hydrate produces in many cases the same chemical reaction as does either sodium or potassium hydrate. Thus, all these bodies produce the same precipitate of ferric hydrate, $Fe(OH)_3$, from a solution of ferric chloride, $FeCl_3$.

The principle of the preparation of ammonia is simply, therefore, to displace it from a salt by the action of a stronger and non-volatile base, such as soda or lime.

22. The composition of ammonia may be determined by introducing a given volume of the gas into a graduated tube over mercury, and passing electric sparks through it. It then decomposes and doubles in volume; and its alkalinity and its pungency, as well as its solubility, disappear.

By eudiometry, that is to say, by the use of a eudiometer, the volumes of the constituents of ammonia may be ascertained in the following way: Assuming that 100 cubic centimeters of ammonia is introduced into a eudiometer, then, on decomposing the ammonia by passing an electric spark through it, the ammonia will be found to have expanded to 200 cubic centimeters; if 100 cubic centimeters of oxygen is then added, and the electric spark again passed through this mixture, the 300 cubic centimeters will be reduced to 75 cubic centimeters, 225 cubic centimeters having apparently disappeared. Of these 225 cubic centimeters, two-thirds, or 150 cubic centi-

meters, must be hydrogen, and 75 cubic centimeters oxygen. Subtracting, now, this excess of oxygen from the original contents of the eudiometer, we have $100 - 75 = 25$ cubic centimeters, which, subtracted from the 75 cubic centimeters remaining in the eudiometer, leaves 50 cubic centimeters. This remainder is nitrogen. Hence, the 200 expanded volumes consists of 150 volumes of hydrogen and 50 of nitrogen; while ammonia gas consists of 3 volumes of hydrogen and 1 volume of nitrogen, the whole condensed into 2 volumes.

23. Tests.—Free ammonia may be easily detected by its well-known penetrating odor, its alkalinity, and the fumes it gives when a rod moistened with hydrochloric acid is brought in close proximity. When combined, it may be set free by quicklime and then tested.

24. Summary.—Ammonia exists in traces in the atmosphere; it is formed by the decomposition of nitrogenous organic matter, and is manufactured from the watery distillate of the gasworks. It is a colorless gas, with characteristic odor, and may be readily liquefied by pressure or cold. It is very soluble in water; is a non-supporter of combustion; and is non-inflammable at ordinary temperatures, but when heated burns with a greenish flame. It is strongly alkaline to litmus solutions, and forms with acids a series of salts in which NH_4 occupies the place of a monad metal.

The group NH_4 has received the name *ammonium*; it does not exist in the free state, but breaks up into ammonia and hydrogen. The composition is determined by decomposing the ammonia gas by electricity and estimating the hydrogen by combining it with oxygen.

25. Laboratory Directions.—In preparing ammonia from the chloride and lime, unless both are dried, there is danger of breaking the flask by water condensing in the upper parts and trickling down on the hot glass. It is a good plan to place two pieces of gauze under the flask and to keep the flame of the Bunsen burner very small. When collecting a gas by displacement, it is advisable to close the mouth of the jar

with a piece of cardboard having a slit through it for the leading tube; this is kept on the mouth until a glass plate, serving as a cover, is exchanged for it.

When the end of the leading tube is placed in the solution (see Experiment 2, Art. 17), watch very carefully that the gas is not absorbed so rapidly as to cause the liquid to rise in the tube; should it have a tendency to do so, increase the heat by turning the Bunsen flame a little higher; if this should not prove effective enough, remove the beaker, and draw the stopper from the flask. In any case, first remove the beaker, and then the flame.

HYDRAZINE AND HYDROXYLAMINE

26. For many years, ammonia was the only known compound of nitrogen with hydrogen. Lately, two others have been discovered, namely, *hydrazine*, N_2H_4 , and *hydroxylamine*, NH_2OH , both of which are very closely related to ammonia. The former is a colorless fuming liquid that boils at $113.5^\circ C.$, solidifies at $0^\circ C.$, and melts at $1.4^\circ C.$ It has a peculiar, pungent odor and a great solubility in water; it reduces silver and copper salts to the metallic state, and forms a hydrate, $N_2H_4 \cdot H_2O$. The latter, produced by reducing nitric acid with tin, forms salts analogous to those formed by ammonia, which have a reducing action like that of hydrazine. It is a white, odorless, crystalline solid that melts at $33^\circ C.$ and boils at $58^\circ C.$ under 22 millimeters pressure. *Hydrazoic*, or *triazonic acid*, HN_3 , discovered by Curtius in 1890, is a highly explosive gas.

OXIDES AND ACIDS OF NITROGEN

27. There are five oxides and three acids of nitrogen. They are as follows:

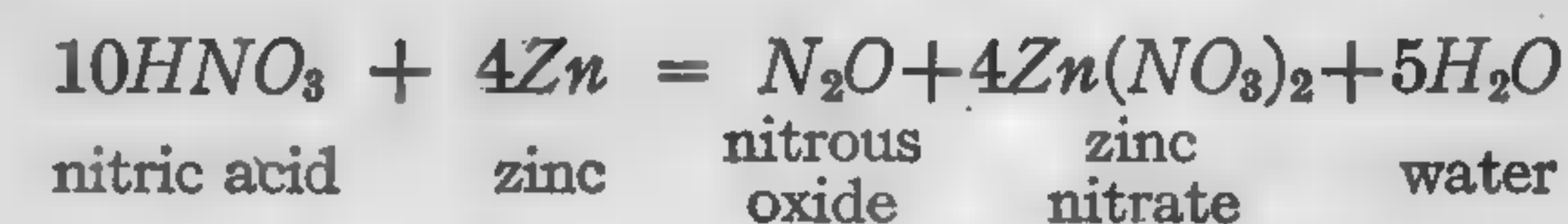
OXIDES		ACIDS	
Nitrous oxide,	N_2O	Hyponitrous acid,	$H_2N_2O_2$
Nitric oxide,	NO		
Nitrogen trioxide,	N_2O_3	Nitrous acid,	HNO_2
Nitrogen peroxide,	NO_2		
Nitrogen pentoxide,	N_2O_5	Nitric acid,	HNO_3

NITROUS OXIDE

Formula N_2O . Density 22.01. Specific gravity 1.5297. Molecular weight 44.02.

28. **History and Preparation.**—Nitrous oxide was discovered by Priestley in 1776; in 1809 it was more accurately examined by Davy, who discovered its exhilarating property. The gas became more widely known in 1845, when Wells began to use it as an anesthetic.

This gas may be prepared by the action of zinc on dilute nitric acid, the two being gently heated together; the reaction is a somewhat complex one, but may be represented by the equation:



It is, however, much more easily obtained by decomposing ammonium nitrate by heat according to the equation:

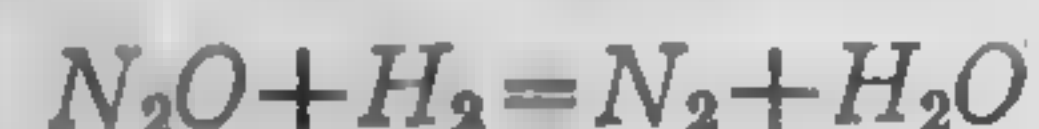


The gas, being heavier than air, may be collected by displacement, or over warm water in a pneumatic trough. It is advisable to place the generating flask in a sand bath and to apply a gentle heat only.

29. **Properties.**—Nitrous oxide is a colorless gas with a faint, sweetish odor and a distinctly sweet taste. It may be condensed to a liquid by a pressure of 32 atmospheres at $0^\circ C.$, or at ordinary pressure at $-88^\circ C.$ The liquid freezes also by its own evaporation when allowed to escape into the open air, producing a snowlike mass. Nitrous oxide supports combustion nearly as vigorously as oxygen; a wax taper having a spark on its wick is relighted in it, much as in oxygen. Phosphorus as well as sulphur burns in it with great splendor, the gas being decomposed, and its oxygen uniting with the combustible, forming oxides, while the nitrogen is liberated. It is quite soluble in cold water, but only very sparingly in warm water; 100 parts of water at $15^\circ C.$ dissolves nearly 78 parts of the gas. It is still more soluble in alcohol and alkaline solutions.

Nitrous oxide acts as an anesthetic when inhaled (that is, it is a substance that causes insensibility to pain). It was with this gas that the property of anesthesia was discovered by Wells, a discovery everywhere acknowledged as the crowning surgical discovery of the 19th century. About 4 or 5 gallons of the gas is sufficient in most cases to produce total insensibility; before this stage is reached, it induces a state of intoxication, often accompanied by violent fits of laughter, owing to which influence it has received the popular name of *laughing gas*.

30. Composition.—The molecule of nitrous oxide, N_2O , yields 1 molecule of nitrogen on decomposition, or any volume of this gas when decomposed yields its own volume of nitrogen. The composition may be determined by exploding the gas in the eudiometer with excess of hydrogen:

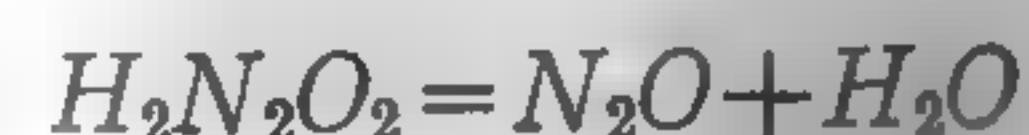


A volume of nitrogen remains, which corresponds to the volume of the nitrous oxide taken, the diminution in volume being due to the hydrogen combining with the oxygen; it is necessary, however, to measure the excess of hydrogen that remains, in order to deduce from this experiment the composition of nitrous oxide.

HYPONITROUS ACID

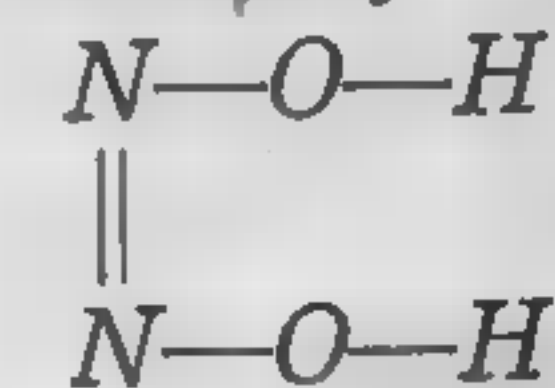
Formula $H_2N_2O_2$. Molecular weight 62.036.

31. By reducing a solution of potassium nitrate with sodium amalgam (a compound of sodium and mercury), potassium hyponitrite is obtained; and, by decomposing silver hyponitrite by hydrochloric acid, the free hyponitrous acid is obtained. It is strongly acid, reduces permanganates, and is iodine free. In water solution it is rather stable, but at ordinary temperatures it slowly decomposes according to the equation:



From this equation it appears that nitrous oxide is the anhydride of hyponitrous acid, though salts of the acid cannot be

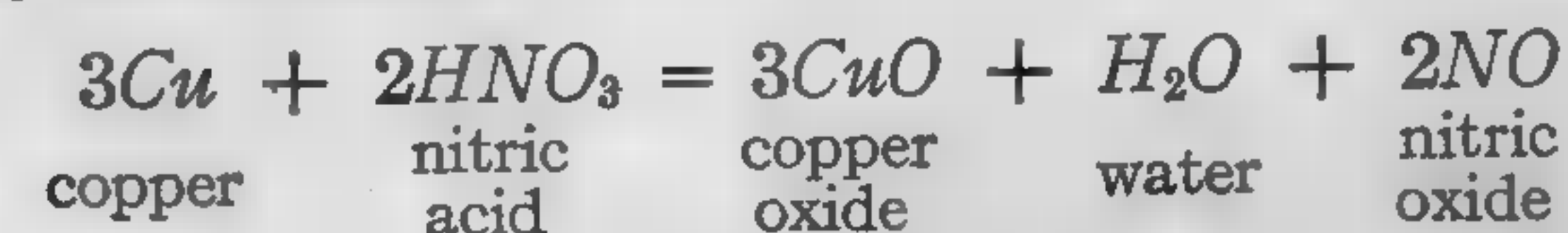
obtained directly from nitrous oxide. When freed from water, hyponitrous acid is a very explosive, white, crystalline solid. Its molecular weight in aqueous solution is 62.036, and its composition is probably correctly represented by the formula



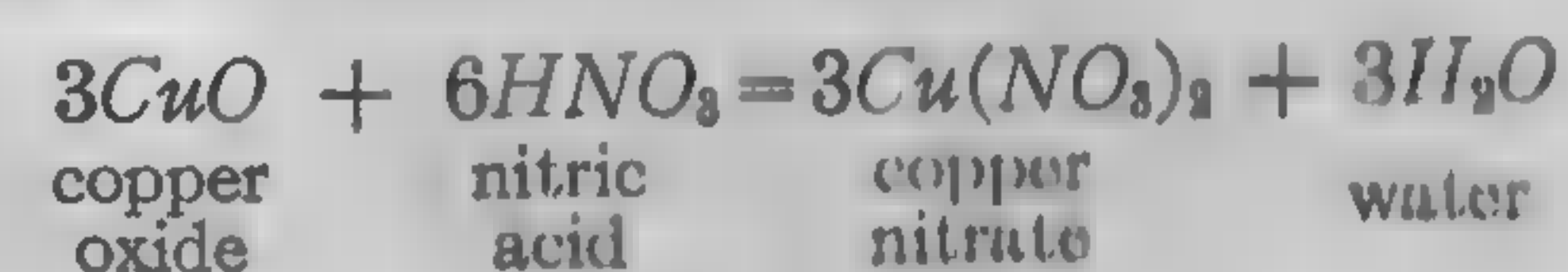
NITRIC OXIDE

Formula NO. Density 15.0. Specific gravity 1.039. Molecular weight 30.01.

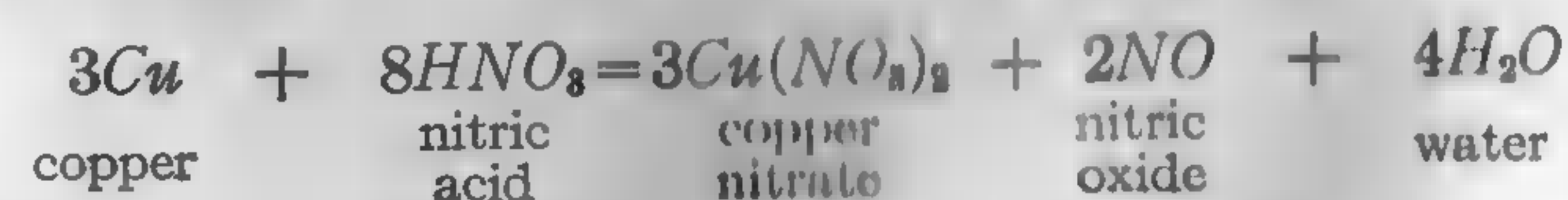
32. History and Preparation.—Nitric oxide, though really discovered by Hales, was first thoroughly investigated by Priestley in 1772. It may be obtained by the action of copper on nitric acid; the reaction occurs without the application of heat. The nitric acid first oxidizes the copper, as shown by the equation:



The copper oxide formed is at once dissolved by the excess of nitric acid, according to the equation:



Or the two reactions may be stated in one equation, thus:



EXPERIMENT.—Place copper clippings in a flask that has a delivery tube. Attach the leading tube to the delivery tube with a piece of rubber tubing about 2 inches long, so that the ends of both glass tubes will be in close contact. (As nitric acid rapidly corrodes rubber, as little as possible of it should be exposed to the influence of the acid.) When a mixture of nitric acid and water, prepared by diluting the acid with twice its volume of water, is poured on the copper, bubbles of gas are evolved, and the generating flask rapidly fills with red fumes. These soon become lighter

in color, and as each bubble of gas rises through the water in the trough into the air, it assumes a dark-red tint. The air is now expelled from the generating flask, and the gas jar may be filled. Should the action slacken before the jar is entirely filled, add some more of the dilute nitric acid.

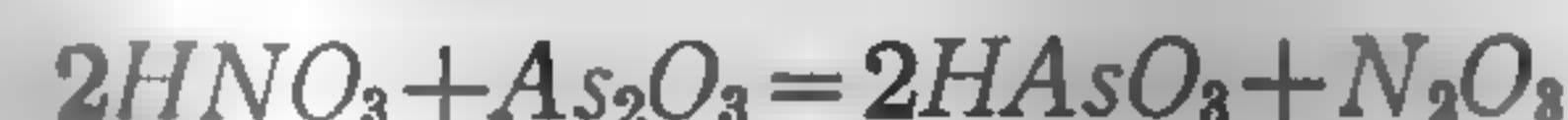
Nitric oxide is prepared also by heating ferrous sulphate and nitric acid. Pure nitric oxide can be readily prepared by the action of a mixture of sulphuric and nitric acids on mercury.

33. Properties.—Nitric oxide is a colorless gas, which, on coming in contact with the air, combines with the oxygen and forms higher nitrogen compounds of a ruddy tint; from its affinity for oxygen it is difficult to either smell or taste it. The strong odor noticed during its preparation is that of these higher oxides, but not that of the nitric oxide. It has almost the same specific gravity as air, namely, 1.039. It is more difficult to liquefy than nitrous oxide, its critical temperature being -93.5°C ., and its freezing point -153°C ., when it solidifies, resembling snow. It is much more stable than nitrous oxide, and may be subjected to even a red heat without suffering decomposition. In consequence of this property, it does not accelerate combustion; a lighted taper plunged into a jar filled with it is immediately extinguished. (Nitric oxide prepared as described in the experiment in Art. 32, however, sometimes contains so much nitrous oxide that a taper burns in it brilliantly.)

NITROGEN TRIOXIDE AND NITROUS ACID

Formulas N_2O_3 and HNO_2 . Molecular weight of the oxide 78.02, of the acid 47.02.

34. Nitrogen trioxide may be prepared by the reduction of nitric acid by arsenious oxide:



By passing the evolved vapors through a freezing mixture, the nitrogen trioxide condenses to a rather unstable greenish-blue liquid that reacts with water, producing *nitrous acid*.

Nitrous acid is a blue liquid, rather unstable at ordinary temperatures, but it may be preserved at a low temperature

unaltered. At ordinary temperatures it is readily decomposed into nitric acid, water, and nitric oxide, thus:

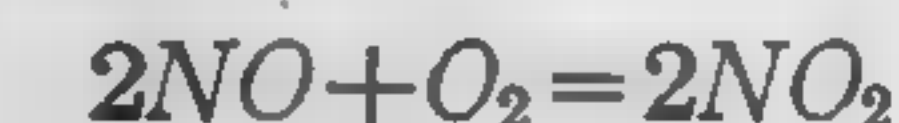


The salts of nitrous acid are known as *nitrites*, and are stable.

NITROGEN PEROXIDE

Formula NO_2 or N_2O_4 .

35. Nitrogen peroxide may be prepared by mixing 2 volumes of nitric oxide with 1 volume of oxygen, when they combine according to the equation:



It is generally prepared by heating perfectly dry lead nitrate, which decomposes thus:



On passing the gases evolved through a freezing mixture, the peroxide is condensed to a liquid, and the oxygen escapes. If perfectly dry, the peroxide congeals to a white crystalline solid at about -9°C . At 0°C the liquid has a faint yellow color that gradually grows darker as the temperature is increased until it is a deep orange at about 24°C ., at which point the liquid boils, evolving an orange vapor.

At very low temperatures the formula of the peroxide is N_2O_4 , but this dissociates in proportion to the temperature until 150°C . is reached, when the formula is NO_2 . N_2O_4 is colorless and NO_2 is colored, so the yellow color at 0°C . shows that dissociation has already commenced, and between this and 150°C . the peroxide is a mixture of N_2O_4 and NO_2 . Above this the formula is NO_2 . Water decomposes the peroxide, the products depending on the temperature. If the water is cold, nitrous and nitric acids are formed, thus:



If the water is hot, nitric acid and nitric oxide are formed, thus:

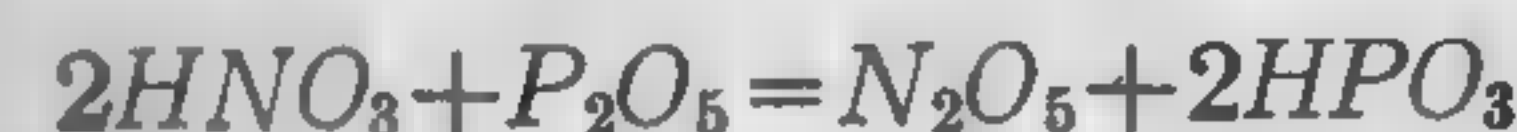


The NO thus formed unites with oxygen of the air, forming NO_2 , and this acts on a further quantity of hot water, as above, until all the oxide is converted into nitric acid. Nitrogen peroxide is an energetic oxidizing agent.

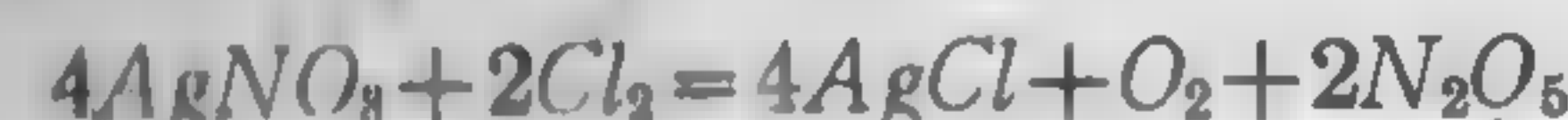
NITROGEN PENTOXIDE

Formula N_2O_5 . Molecular weight 108.02.

36. Nitrogen pentoxide, which was first prepared by Deville in 1849, may be prepared by treating nitric acid with phosphorus pentoxide, a substance that has a strong affinity for water, when the following reaction takes place:



It is more readily obtained by passing chlorine over silver nitrate and condensing the product. The reaction is:



Nitrogen pentoxide is a colorless, transparent solid that crystallizes in right rhombic prisms. It melts at 30°C . and boils at 47°C . It is very unstable, sometimes exploding spontaneously. It reacts energetically with water, producing nitric acid, according to the equation:



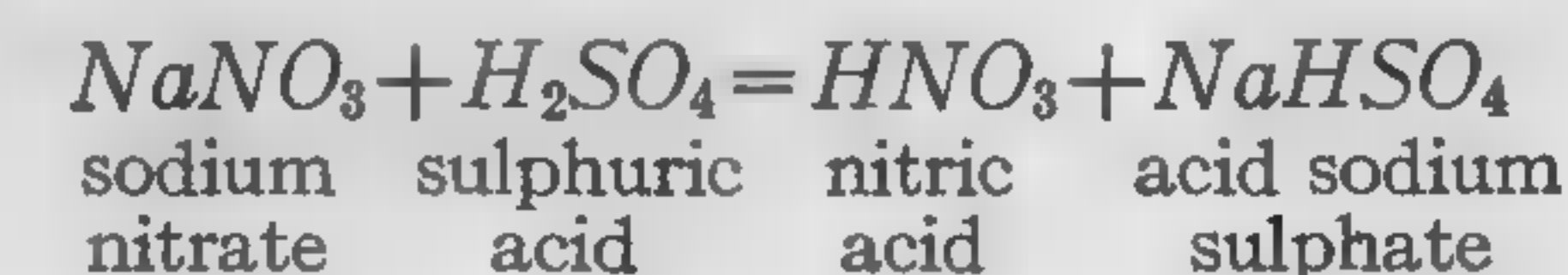
NITRIC ACID

Formula HNO_3 . Density 31.509. Molecular weight 63.018.

37. History and Occurrence.—Nitric acid was known to Geber, an alchemist, who lived in the 8th century; Raymond Lully in 1225 described a method of preparing it; and in 1785 Cavendish thoroughly investigated this compound and determined its composition synthetically. It exists in small quantities in the atmosphere, from which it is separated by rain, which, consequently, usually exhibits, on analysis, traces of this acid. The salts of nitric acid, with sodium and potassium (sodium and potassium nitrates), are its most common sources.

Layers of potassium nitrate are found incrusting the soil in India, and of sodium nitrate in parts of Peru and Chile. These nitrates are produced by the oxidation of nitrogenous organic matter in the presence of the bases potash or soda. Potassium nitrate is also known as *saltpeter*, or *niter*; sodium nitrate is frequently called *Chile saltpeter*, or *cubic niter*, from the shape of its crystals.

38. Preparation.—Nitric acid is always produced by the distillation of a nitrate—generally sodium or potassium nitrate—with sulphuric acid. The two are mixed in a retort, and on the application of heat, nitric acid, being volatile, distils over, leaving acid sodium sulphate. The reaction may thus be represented:



EXPERIMENT.—Pour about 20 grams (20 cubic centimeters of the measuring glass) of sodium nitrate through the tubulure of a clean, dry, stoppered retort. This is most easily done by folding a piece of paper as shown

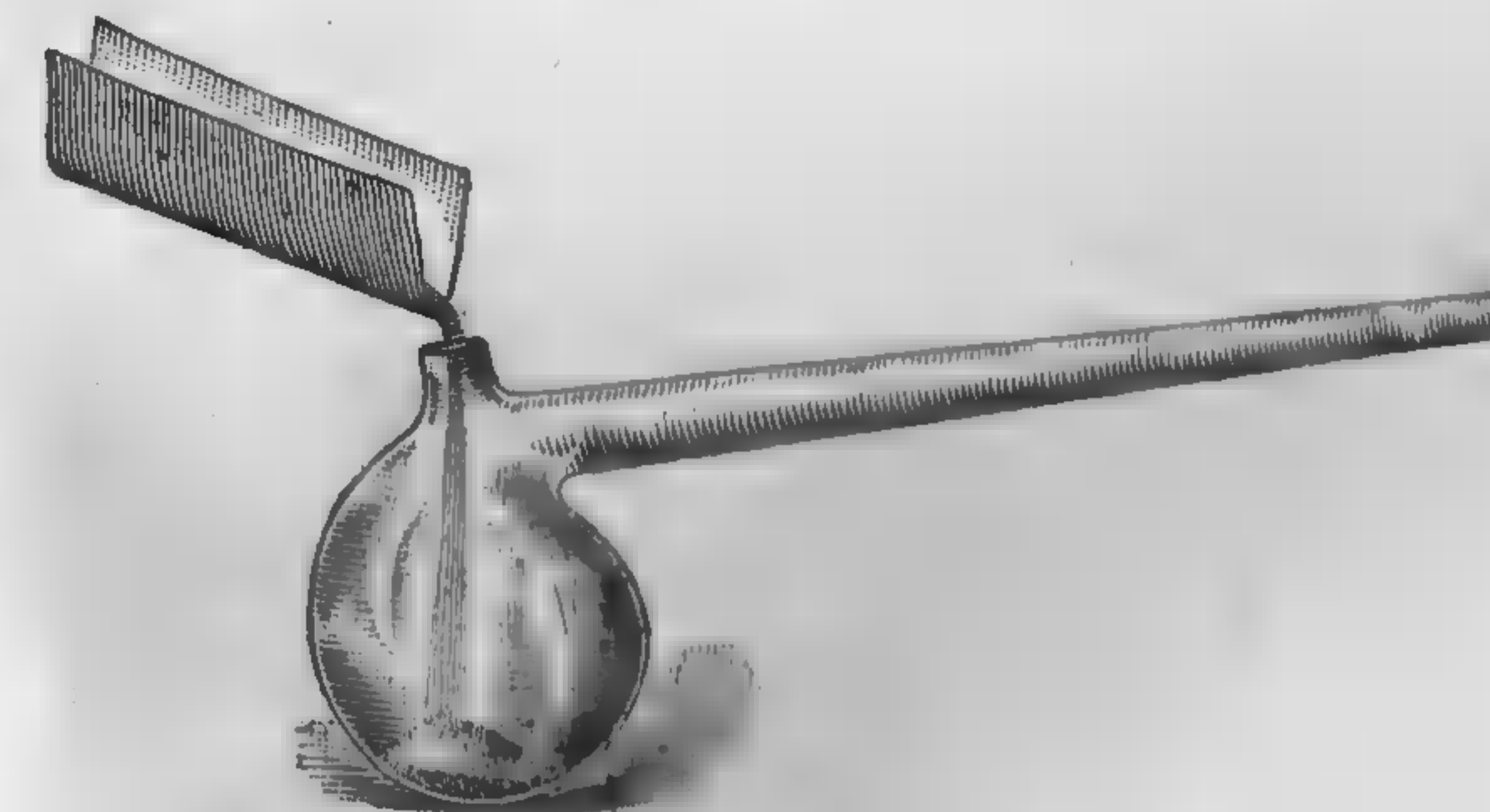


FIG. 6

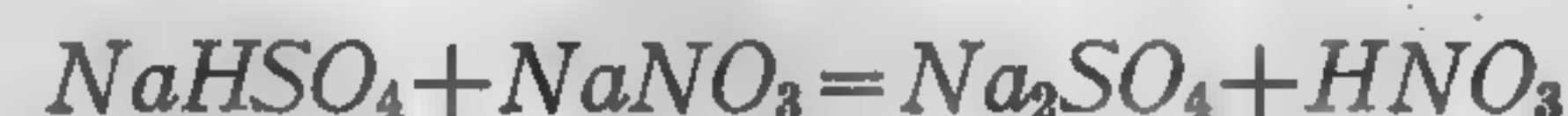
in Fig. 6; the sodium nitrate is placed on this and carefully transferred to the retort, which should be held as shown in the figure; on no account must any of the nitrate get into the neck of the retort.

Next clean and drain a receiver, and introduce into it the beak of the retort, as shown in Fig. 7. Arrange the apparatus in the retort stand with the receiver well under water in the pneumatic trough; the farther the receiver is submerged in cold water the better. To get up this arrangement satisfactorily, it may be necessary to raise the pneumatic trough somewhat; adjustments of this kind are best made by pieces of wood

(blockings); the trough should be put in the proper place, and then filled with water. Next pour in the retort about 15 cubic centimeters of concentrated sulphuric acid, replace its stopper, and apply heat carefully with the Bunsen burner.

The nitrate soon melts, the retort becomes filled with brownish-red fumes, and a pale yellow liquid, HNO_3 , distils over into the receiver.

If two molecules of sodium nitrate are used to one of sulphuric acid and the temperature is increased, the resulting acid sulphate is decomposed as follows:



The temperature required for this reaction frequently decomposes a part of the nitric acid formed.

39. Properties.—Nitric acid, when pure, is a colorless, fuming, corrosive, and strongly acid liquid, but usually has a faint yellow tinge, owing to the presence of some of the lower

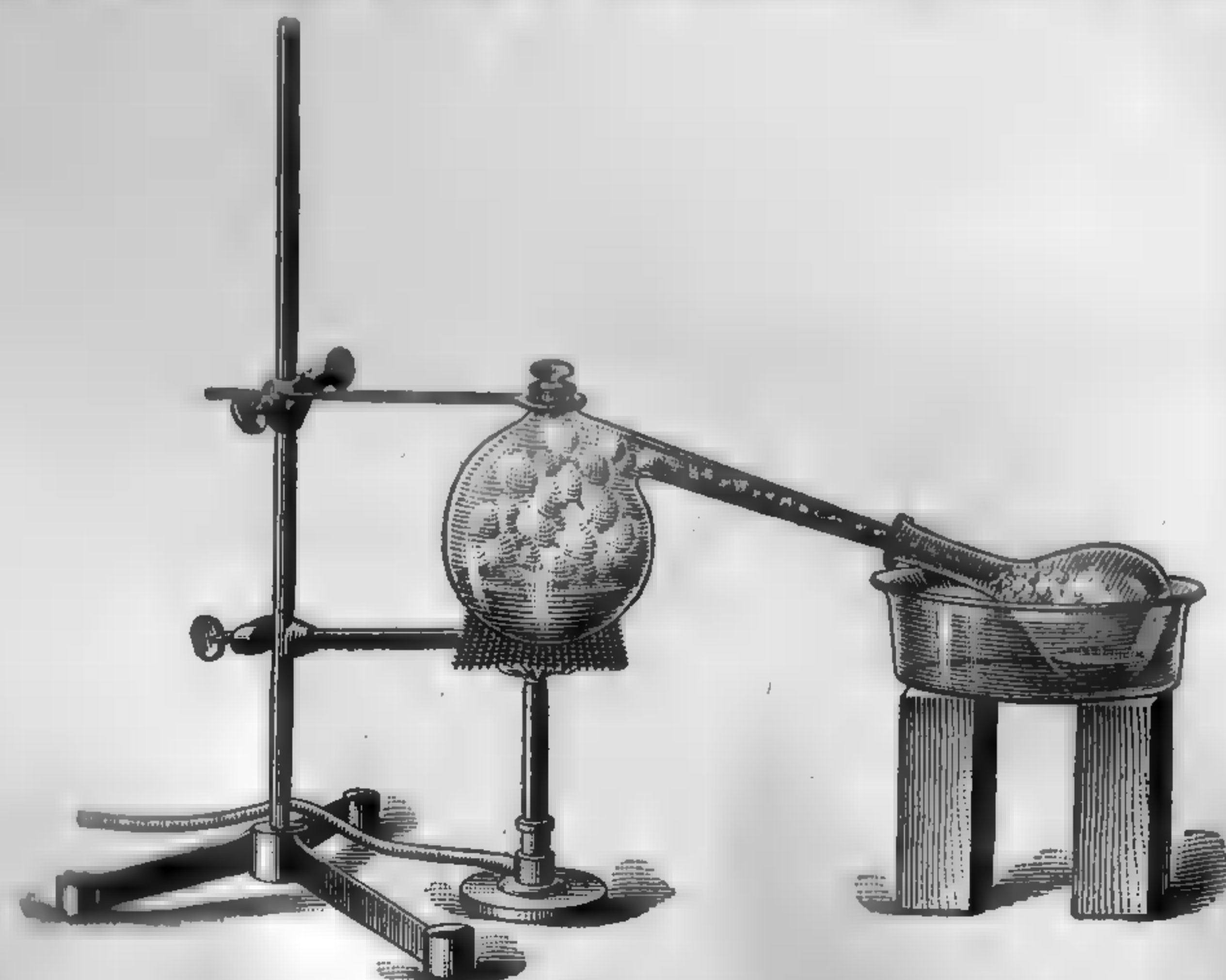


FIG. 7

oxides of nitrogen, produced by its partial decomposition. Cooled to $-47^\circ C.$, the acid freezes, and heated to $86^\circ C.$, it boils, undergoing partial decomposition. It is also readily decomposed by light. Chemically, it is a powerful oxidizing agent, acting on most of the metals with great vigor; gold and platinum, however, are not affected by it. Nitrogenous animal

substances, such as parchment, silk, horn, and wool, are colored yellow by it, while any non-nitrogenous vegetable substances, such as cotton, sugar, glycerine, etc., are converted into violently explosive bodies.

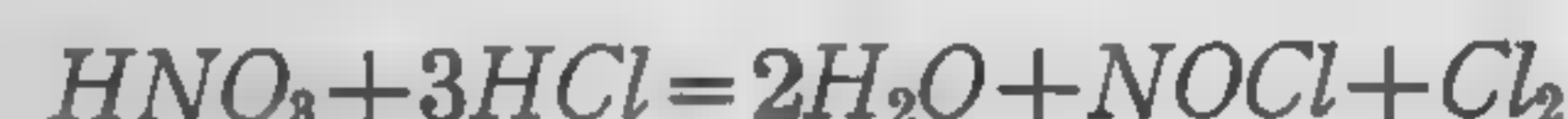
The commercial nitric acid—sometimes sold as *aqua fortis*—is of two sorts, called *single* and *double*. Double aqua fortis is the ordinary concentrated acid of commerce, has a specific gravity of 1.42, and contains about 67 per cent. of HNO_3 ; the single has a specific gravity of 1.29, and contains about 46 per cent. of the pure acid.

Nitric acid, being a monobasic acid, can form only normal salts, which may be represented by the formula $M(NO_3)$, M standing for any monad metal. When free, nitric acid reddens litmus powerfully, bleaches indigo solutions, and evolves red fumes on introducing a little copper. Nearly all the non-metallic elements, sulphur, phosphorus, carbon, etc., are oxidized to their acids by it. The reactions of free nitric acid are also obtained from nitrates after treatment with sulphuric acid. Moreover, nitrates deflagrate (that is, undergo a vigorous combustion) when thrown on burning charcoal.

40. Uses.—Nitric acid finds wide use in the arts. It is employed for etching on metals, for oxidizing various substances, for forming certain substitution products, such as nitrobenzol and picric acid, and for the preparation of explosives, such as guncotton, nitroglycerine, etc. As all the metals in common use, except gold, platinum, and aluminum, are attacked by it, this acid is employed to distinguish and separate the first two metals from others of less value. The ordinary method of ascertaining whether a trinket is made of gold consists in touching it with a glass stopper wetted with nitric acid, which leaves gold untouched, but colors base alloys blue, from the formation of copper nitrate. The *touchstone* allows this method of testing to be applied with great accuracy. It consists of a species of black basalt, obtained chiefly from Silesia. If a piece of gold is drawn across its surface, a golden streak is left, which is not affected by moistening with nitric acid; while the streak left by brass, or any similar base alloy, is readily dissolved by

the acid. Experience enables an operator to determine, by means of the touchstone, pretty nearly the amount of gold present in an alloy, comparison being made with the streaks left by gold alloys of known composition.

41. Aqua Regia.—Neither nitric acid nor hydrochloric acid alone has the property of dissolving gold; but a mixture of 1 volume of nitric and 3 volumes of hydrochloric acid, to which the name aqua regia has been given, readily dissolves gold. This property of dissolving gold depends on the presence of free chlorine, which is liberated in the action of the acids on each other, as shown in the equation:



42. Action of Nitric Acid and Nitrates.—The action of nitric acid on the metals is generally more complex than the action of hydrochloric or sulphuric acid; it first oxidizes the metal, a portion of the acid being reduced, liberating one or more of the lower oxides of nitrogen, the remaining nitric acid dissolves the oxide of the metal forming a nitrate and water. The particular oxide evolved, and the proportions of each present in a mixture, depend on the metal used, the degree of concentration of the acid, and various other causes.

EXPERIMENT 1.—To some of the nitric acid obtained by the experiment in Art. 38, add a few pieces of copper clippings; notice that a violent action goes on, ruddy fumes are evolved, and a green solution of copper nitrate is formed.

Nitric acid is a monobasic acid, its salts being known as *nitrates*. These nitrates may be prepared either by the action of the acid on the metal, as with copper in the last experiment, or by adding the acid to an oxide or carbonate.

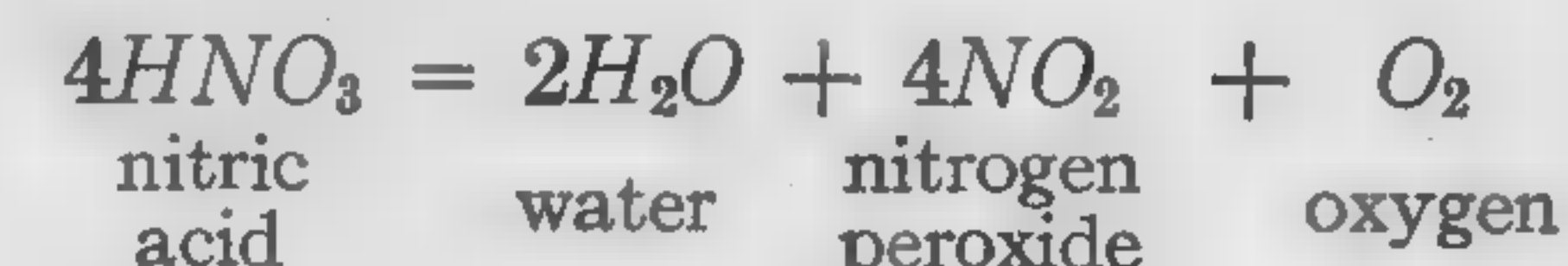
EXPERIMENT 2.—Place some strong nitric acid in a beaker, and add some solid ammonium carbonate in small quantities, until it no longer causes effervescence; the liquid will then have an alkaline reaction to litmus paper. Add nitric acid, drop by drop, until the solution is neutral; place this away for a week in an evaporating dish; at the end of that time long needles of ammonium nitrate will have crystallized out. The salt may be preserved in a bottle for future use.

The nitrates, like the acid from which they are derived, are powerful oxidizing agents; potassium nitrate is used as a source of oxygen in gunpowder, which is a mixture of that compound with sulphur and charcoal.

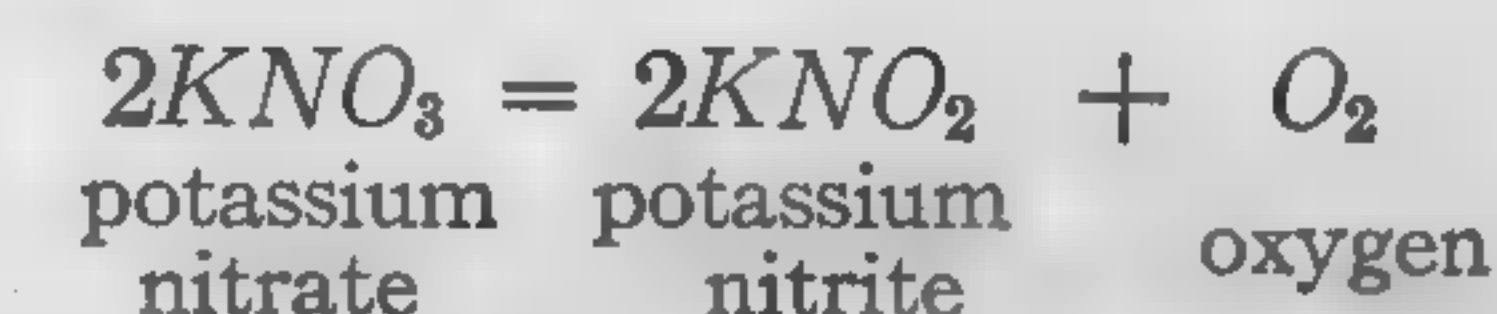
If charcoal is dropped into melted potassium nitrate it takes fire and burns with great brilliancy.

EXPERIMENT 3.—Melt some potassium nitrate in a test tube, and drop in a fragment of charcoal; it burns with the evolution of carbon dioxide. The mouth of the tube should be held away from the body, as sometimes the red-hot piece of charcoal jumps out of the tube.

By heat, nitric acid and all the nitrates are decomposed; the metallic oxides remain, while the oxides of nitrogen as well as oxygen are driven off. A good example of this is given in the reaction that takes place when nitric acid is passed through a red-hot tube of clay.



or, when potassium nitrate is heated, the following change occurs:



43. Summary.—Five oxides and three acids of nitrogen are known. Nitric acid is the most important; traces of it exist in the atmosphere. It is manufactured from nitrates by distillation with sulphuric acid. It is a powerful oxidizing agent; though it attacks most of the metals, it has no action upon gold or platinum, which, however, may be dissolved by aqua regia. Nitrous oxide, or laughing gas, is usually prepared by heating ammonium nitrate. It is colorless, has a faint sweetish odor and a distinct sweetish taste; is somewhat soluble in water, is non-inflammable but supports combustion. It acts as an anesthetic. Nitric oxide is prepared by the action of copper on nitric acid. It is colorless, but on exposure to air immediately becomes red by combination with oxygen. It is more stable than nitrous oxide, and does not support combustion, unless the heat is sufficient to decompose it into oxygen

and nitrogen. The other oxides and acids are comparatively unimportant.

44. Laboratory Directions.—Wooden blocks for the adjustment of the height of different pieces of apparatus are always useful in a laboratory, and should be at hand. Blocks 6 inches square are a convenient size, and the following thicknesses may be kept in store: $\frac{1}{2}$, 1, 2, 3, and 4 inches. They may be obtained at very small expense from any carpenter.

The flask used for the preparation of nitrous oxide should not be less than 8 ounces, as otherwise some of the melting nitrate may froth up and choke the tube; should any do so, immediately remove the light, as the continued evolution of gas might burst the flask. If the applied heat is too great, the gas comes over impure; and if it is cloudy in the jar, that may be looked upon as a sign that the heat must be moderated.

The action of copper on nitric acid does not always start immediately; when this is the case, apply a very gentle heat to the flask until the action commences. As it is liable then to proceed with great rapidity, a large generating flask should be used. If the gas is coming over too fast, pour in a little water; this will render the action less violent. The stopper and tubing used should be washed immediately after use. The directions for the protection of the stopper and tubing are important; if a long piece of rubber tubing is used as connection, the tubing is not only destroyed, but also becomes stopped with the products of corrosion. It is a good plan, in this particular case, to have the leading tube bent out of one piece of glass tubing; but, if there is a joint, provided the ends of both glass tubes touch each other, as directed, it will not matter much.

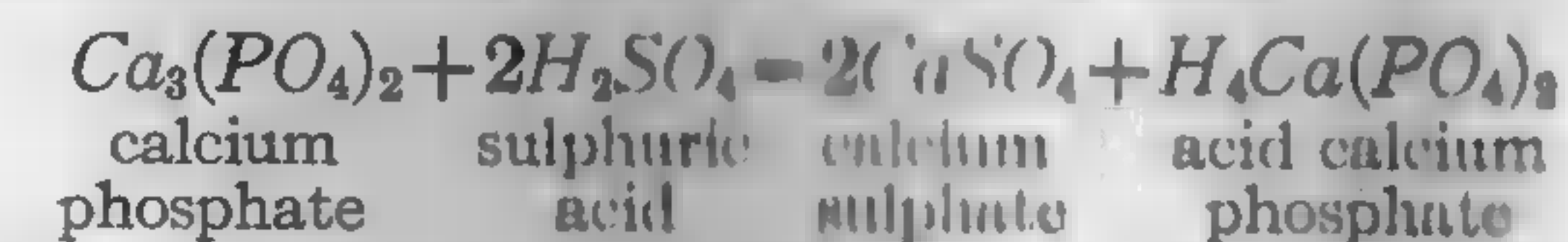
In adding ammonium carbonate to nitric acid, do not throw it in in the form of fine powder, as the action is then so violent that it is likely to overflow the beaker. Pieces about the size of peas are the most convenient for this experiment.

PHOSPHORUS

Symbol P. Atomic weight 31.04. Density 62.08. Valence III and V. Specific gravity 1.83. Molecular weight 124.16.

45. History and Occurrence.—Phosphorus was first obtained by Brand, of Hamburg, in 1670, by strongly heating a mixture of evaporated urine and white sand in an earthen retort. In 1775 Scheele found it could also be made from bones. Phosphorus derives its name from the Greek word meaning light bearer, from its property of giving light in the dark. Owing to its great affinity for oxygen, it is never found free in nature. It is, however, very widely distributed, and is found abundantly in the form of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. The minerals containing phosphates are subject to disintegration, and thus phosphorus is allowed to pass into the soil, from which it is extracted by plants. No plants will grow in a soil destitute of phosphorus, as it is required to build up certain parts of plant structure, particularly the fruit and seeds. As animals feed on plants, the phosphorus enters into their bodies, hence it occurs in the bones of animals, which contain about three-fifths of their weight of calcium phosphate.

46. Preparation.—Phosphorus is the only element for the ordinary preparation of which animal substances are employed. "It is prepared by acting upon burned bones with sulphuric acid, leaching off the resulting liquid, evaporating it to dryness, and distilling the residue with charcoal. The earthy matter of bones consists of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, and, by treating this with sulphuric acid, acid calcium phosphate results, according to the following equation:



The acid calcium phosphate is leached off from the insoluble calcium sulphate, and by evaporating to dryness, is converted into calcium metaphosphate, thus:



and the calcium metaphosphate distilled with charcoal gives phosphorus and calcium phosphate again, according to the equation:



In the manufacture of phosphorus on a large scale the organic material in the bones is made use of in several ways. The bones are boiled with water, or treated with superheated steam, to extract the gelatin. Sometimes they are heated in iron retorts to distil off the ammonia and other volatile substances they contain. If the latter procedure is followed the residue

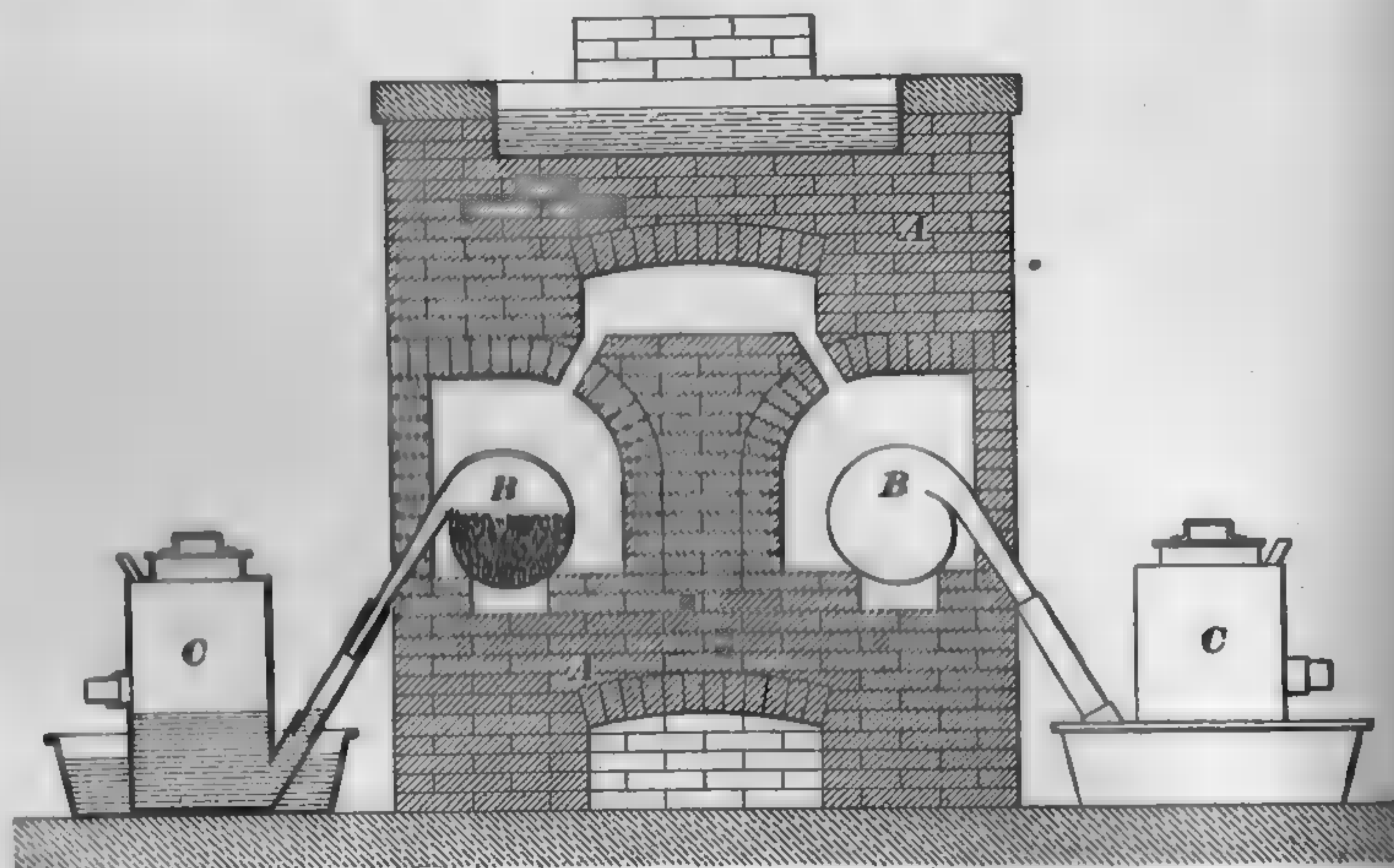


FIG. 8

remaining after the distillation consists of bone black, bone coal, or animal charcoal, which is used in the manufacture of sugar syrups and various other articles. After the animal charcoal has become useless for these purposes it is completely burned in an open fire and thus converted into bone ash. To prepare phosphorus, the bone ash is mixed with two-thirds of its weight of strong sulphuric acid diluted with 18 to 20 parts of water, well stirred, and allowed to stand for about 12 to 14 hours. The clear liquid is strained off the sediment, which consists of calcium sulphate, evaporated in a pan to a sirupy consistence, mixed with one-fifth of its weight of charcoal, finely powdered, and heated to redness. The dry mass is then

placed in earthen retorts *B*, Fig. 8, which are slowly raised to bright redness in the furnace *A*, when the phosphorus distils over and condenses in the receivers *C*. Theoretically, the bone ash should yield about 11 per cent. of phosphorus, but practically hardly more than from 8 per cent. to 9 per cent. is obtained.

The crude phosphorus is purified by enclosing it in a chamois-skin sack, and strongly compressing it under water at 50° C.; the phosphorus passes through the leather and collects under the water. It is molded into sticks by being drawn into slightly conical glass tubes, which are then plunged into cold water. The phosphorus solidifies and is easily drawn from the tubes.

Phosphorus is prepared also by an electrical process known as the Readman, Parker, and Robinson system, in which the calcium phosphate is converted directly into phosphorus without previous treatment with sulphuric acid. The phosphate is mixed with charcoal and other fluxes, heated to as high a temperature as possible, and then introduced into an electrical furnace. The electrical furnace used consists of an iron tank lined with refractory material, and contains large carbon electrodes in the sides. At the high temperature thus attained phosphorus vapor mixed with other gases passes over and is condensed. The slag formed is drawn off at intervals and fresh material charged into the furnace, thus making the process continuous.

47. Properties.—Phosphorus is distinguished from all the other elements so far considered, in that it has 4 instead of 2 atoms in the molecule. This, however, does not mean that the molecule of phosphorus is twice the normal volume of other elements, which would be a contradiction of Avogadro's law, but simply that, with the same molecular volume as other bodies in the gaseous state, the phosphorus molecule contains 4 atoms.

Phosphorus is an almost colorless (slightly yellow), transparent solid, that has a specific gravity of 1.83, with a consistency of beeswax at ordinary temperatures, and may be easily cut with a knife. At the freezing point it becomes

considerably harder and more brittle; it then shows, on being broken, evidences of crystalline structure. Phosphorus melts at 44°C . to a colorless liquid, and boils at 290°C ., yielding a colorless vapor of specific gravity 4.355. It crystallizes from its solution in carbon disulphide in the form of the regular dodecahedron. When exposed to the air, phosphorus is seen to evolve small quantities of smoke, and in the dark is distinctly luminous, though a trace of naphtha or oil of turpentine in the air prevents this phenomenon. It is not soluble in water, but dissolves readily in carbon disulphide, in phosphorus chloride, slightly in alcohol, and in ether, and in certain volatile oils. It is characterized by its great inflammability; at a temperature a little over its melting point it takes fire, and burns brightly with the formation of phosphorus pentoxide. Phosphorus is easily ignited by slight friction.

Owing to the readiness with which it undergoes oxidation, phosphorus is always kept under water, which liquid it does not decompose. Phosphorus is violently poisonous, and kills by depriving the blood of oxygen. Oil of turpentine is the best antidote. Heated to 50°C . in the air, it takes fire and burns vividly, forming phosphorus pentoxide.

48. Red, or Amorphous, Phosphorus.—In addition to the yellow variety, phosphorus occurs in another totally distinct form, known as red, or amorphous, phosphorus. Schroedter, in 1848, discovered that, by heating ordinary phosphorus to 300°C . in a gas that had no direct action on this element, or in sealed tubes, the phosphorus was converted into a red powder that possessed properties entirely different from those previously exhibited.

This modification differs most remarkably from the yellow kind. It is a dull carmine-red, tasteless, powder with a specific gravity of 2.14, and is not poisonous. It is insoluble in the ordinary solvents of phosphorus, but may be dissolved in metallic lead by being heated in a sealed tube together with this metal. On cooling, it crystallizes out in acute rhombohedral crystals having a metallic luster, an almost black color, and a specific gravity of 2.34. It has no odor, is not luminous when

exposed to air, does not oxidize, and, consequently, need not be preserved under water. It remains solid up to a temperature beyond 250°C ., and does not take fire when heated in the air until 260°C . is reached. At about this point it changes into the yellow variety and burns.

If the heating is conducted in a retort filled with carbon dioxide, so as to prevent combustion, the same weight of yellow phosphorus is produced, which proves most convincingly that the two varieties are only allotropic modifications of one and the same element. Further, both, on being burned, produce the same weight of phosphorus pentoxide, P_2O_5 .

The change from the yellow to the red variety is much accelerated by the presence of iodine in small quantities.

EXPERIMENT.—Place a piece of phosphorus about the size of a pea in a test tube; drop on it a very small fragment of iodine; combination at once occurs, with the formation of a small quantity of phosphorous iodide. Heat gently; the phosphorus melts and takes fire, but soon exhausts the air in the tube. Continue to warm gently for a time, and most of the phosphorus will become a dark-red color. Stopper the test tube and allow it to cool. When quite cold, pour some carbon disulphide into another tube, and put away the bottle; then from the tube pour the disulphide on the altered phosphorus. Stopper again, and allow the tube to stand for some time, giving it an occasional shake. Pour off the carbon disulphide, and a residue of amorphous phosphorus remains.

49. Uses.—Phosphorus is extensively used in the manufacture of matches, and also finds employment in medicine and the production of rat poison. Its spectrum is characterized by two green lines, readily seen in the flame of hydrogen that has been passed over phosphorus.

50. Matches.—The first matches were made about the year 1827. Up to this time fire had been artificially obtained by rubbing together a piece of hard wood and a piece of soft wood. This was followed by the tinder and flint. The first matches were made of pieces of wood, the ends of which had been dipped into sulphur and coated with a mixture of sugar and potassium chlorate. These matches were ignited by being dipped into a bottle containing asbestos moistened with fuming sulphuric acid. Later the sulphured ends of the matches were

dipped in a mixture of antimony sulphide and potassium chlorate made into a paste with gum. These were ignited by drawing between two pieces of sand paper. Phosphorus soon replaced the sulphide of antimony, and potassium nitrate was substituted for the chlorate, thus overcoming the danger of an explosive ignition. Another improvement was the substitution of wax for sulphur, overcoming in this way the disagreeable odor due to the burning sulphur.

The discovery of red phosphorus and its non-poisonous character led to the use of this substance in the manufacture of matches. This substance has been found very valuable, as its use overcomes the phosphorus disease caused by the use of the white phosphorus. In fact, at this time it is unlawful to use white phosphorus in the manufacture of matches.

The Swedish, or safety, matches are tipped with a mixture of potassium chlorate, potassium bichromate, red lead, and sulphide of antimony. This mixture will not ignite by simple friction, but will ignite when rubbed upon a mixture of red phosphorus and finely ground glass, spread on the sides of the box.

PHOSPHORUS AND HYDROGEN

51. Four compounds of phosphorus and hydrogen are known: PH_3 , a gaseous compound similar in composition to ammonia; PH_2 , or P_2H_4 , a liquid compound corresponding to hydrazine; P_4H_2 , and P_9H_2 , solid compounds.

52. **Phosphine**, which is sometimes called *phosphureted hydrogen*, was discovered in 1783 by Gengembre, and further investigated by Heinrich Rose in 1832. It has a density of 17.02, a specific gravity of 1.17, and a molecular weight of 34.064. Its formula is PH_3 . It is a very poisonous gas, producing death even when present in small quantities in respired air.

On boiling a strong solution of sodium or potassium hydrate with phosphorus, a gas is evolved, having the odor of putrid fish, and approximately the composition PH_3 . This gas is phosphine.

EXPERIMENT.—Fit up a retort with a delivery tube, with its end leading into a pneumatic trough, as shown in Fig. 9, and arrange the whole in a

retort stand. Introduce into the retort a few fragments of potassium hydrate, together with some small pieces of phosphorus and a little water. Pass coal gas through the tubulure, so as to completely displace the air; then close the tubulure tightly. Gently heat the retort; bubbles of gas soon rise and displace the coal gas. In a short time, each bubble, as it rises to the surface of the water in the pneumatic trough, bursts into

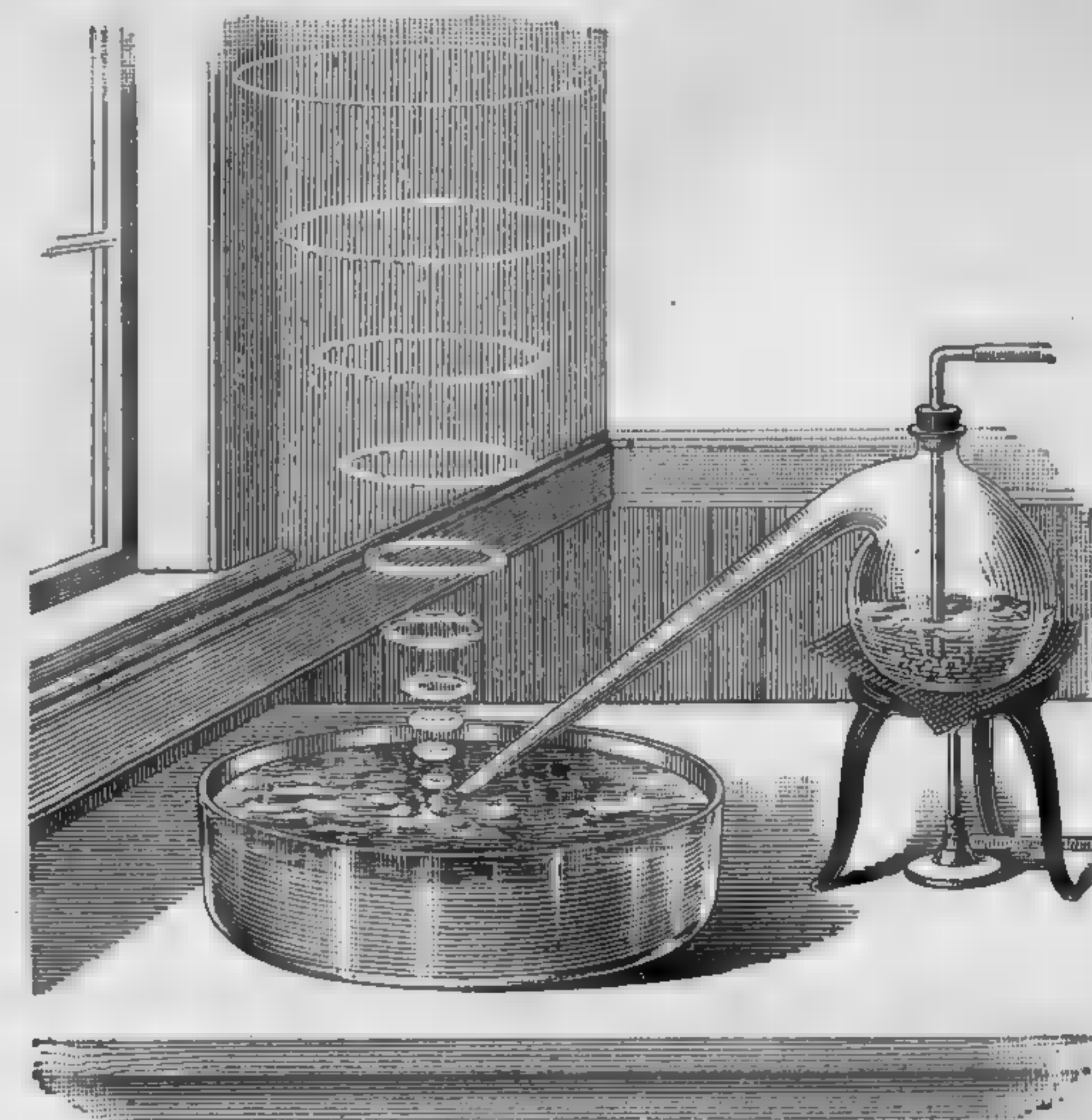
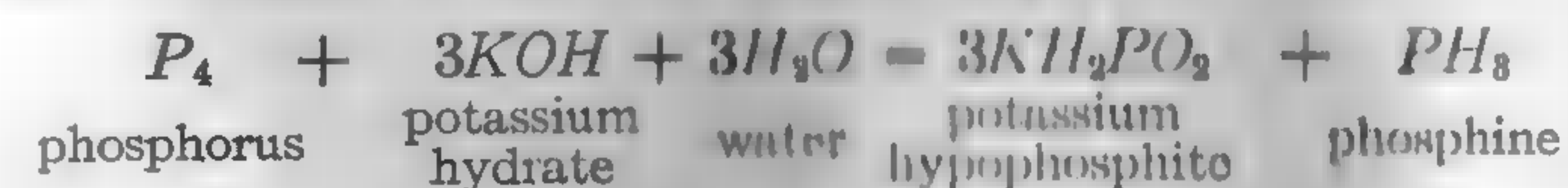


FIG. 9

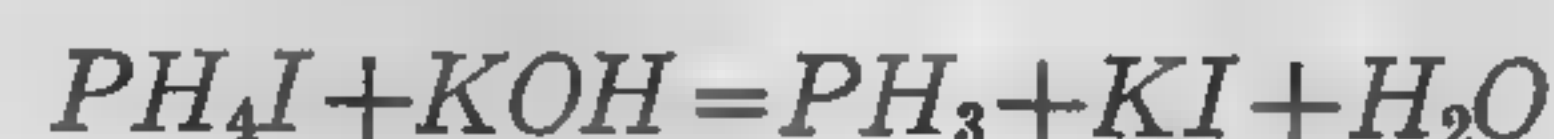
flame and generates an extremely beautiful ring of white smoke which rotates on its circular axis as it ascends. If the air of the room is still, several of these rings will follow one another up to the ceiling.

The reaction by which phosphine is thus produced is a somewhat complicated one, but may be expressed thus:



In addition to phosphine, PH_3 , traces of P_2H_4 are formed, which cause the gas to inflame spontaneously. If the gas is collected in a jar, on standing, it loses this property of spontaneous inflammation, because the second phosphide, P_2H_4 , suffers decomposition. In this method of preparing the gas, milk of lime (that is, calcium hydrate suspended in water) may be employed instead of potassium hydrate.

Pure phosphine is best obtained by the decomposition of phosphonium iodide, PH_4I , by means of potassium hydrate, thus:



Phosphine is a colorless gas with an unpleasant odor of putrid fish. It is sparingly soluble in water, is condensable to a liquid at $-85^\circ C.$, and is neutral in its reactions. It takes fire readily at $100^\circ C.$, burning with a brilliant flame, but is not a supporter of combustion. The aqueous solution of phosphine decomposes in the light into hydrogen and red phosphorus. Phosphine is absorbed by solutions of copper sulphate and mercuric chloride, forming phosphides of the metals. It possesses, like ammonia, the property of combining with certain metallic chlorides, such as aluminum chloride, stannic chloride, and antimony chloride.

53. Liquid phosphine, P_2H_4 , was discovered by Thénard in 1845. It is obtained simultaneously with gaseous phosphine, from which it is separated by cooling. It is a colorless, strongly refractive liquid, and has a specific gravity of 1.012. It is spontaneously inflammable, burning with great brilliancy to phosphorus pentoxide, and boils at $57^\circ C.$, leaving no residue if not heated to too high a temperature. On heating above its boiling point or on exposure to light, liquid phosphine decomposes into gaseous and solid phosphine.

54. Solid Phosphines, P_4H_2 and P_3H_2 .—The compound P_4H_2 is formed by the decomposition of liquid phosphine, as just stated, or by means of hydrochloric acid. It forms a yellow powder that burns when heated to $160^\circ C.$, and has feeble acid properties. Heated to $70^\circ C.$ in a stream of carbon dioxide it decomposes into hydrogen and phosphorus. When heated in a vacuum pure phosphine is evolved and there remains a residue of a red substance having the formula P_3H_2 , thus:



55. Phosphonium Compounds.—Phosphine acts like ammonia and combines with hydrobromic and hydriodic acids, forming salts. In these salts the group PH_4 acts like a metal and is termed *phosphonium*, just as the group NH_4 is called

ammonium. The phosphonium compounds are not as stable as the ammonium compounds.

Phosphonium bromide, PH_4Br , is formed when hydrobromic acid and phosphine are brought together. The vapor has a specific gravity of 1.906. The bromide crystallizes in colorless cubes, and boils at $30^\circ C.$

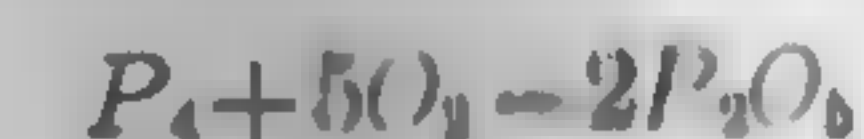
Phosphonium iodide, PH_4I , is best prepared by adding yellow phosphorus to a saturated solution of hydriodic acid and after allowing this to stand for some hours, adding some iodine. It can also be prepared by decomposing phosphorus di-iodide with a small quantity of water. The iodide forms large, transparent, glittering, quadratic prisms, fumes in the air, boils at $80^\circ C.$, but it easily vaporizes at lower temperatures. It is easily decomposed with water. Phosphonium iodide is used as a powerful reducing agent and as the basis for the preparation of many organic phosphorus compounds.

OXIDES AND ACIDS OF PHOSPHORUS

56. The common oxides and acids of phosphorus are as follows:

OXIDES	ACIDS
Phosphorus trioxide, P_2O_3	Hypophosphorous acid, H_3PO_2
Phosphorus pentoxide, P_2O_5	Phosphorous acid, H_3PO_3
	Metaphosphoric acid, HPO_3
	Orthophosphoric acid, H_3PO_4
	Pyrophosphoric acid, $H_4P_2O_7$

57. Phosphorus pentoxide, whose formula is P_2O_5 and whose molecular weight is 142.08, is always the product of the rapid combustion of phosphorus in the air or in oxygen. The reaction, which is synthetic, may be expressed by the equation:

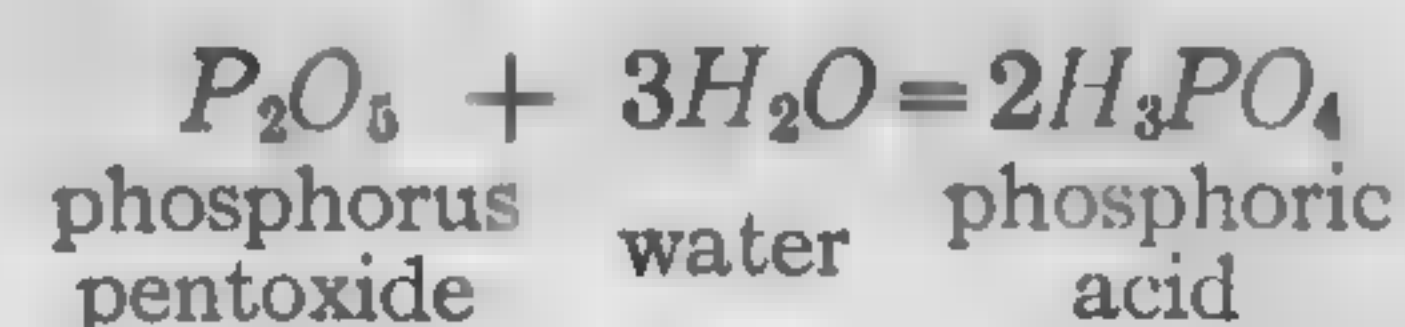


EXPERIMENT.—Place under a large bell jar a flat china dish containing sulphuric acid, and leave this standing for about an hour or two, so as to dry thoroughly the air under the bell jar. Then remove the dish carefully, without disturbing the air within the jar. A fragment of phosphorus about the size of a small pea, carefully dried between two pieces

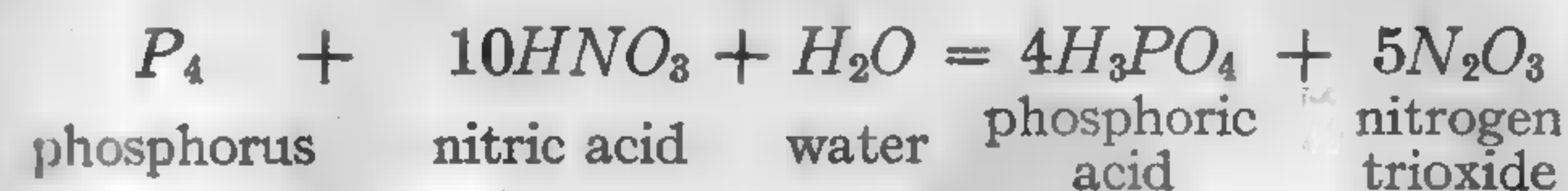
of blotting paper, is placed in a china saucer standing on a good-sized plate of glass and introduced under the bell jar, the phosphorus having been kindled with a hot wire. White fumes will fill the jar, come together, and fall into the saucer and on the glass plate, resembling in appearance a miniature snow storm.

Phosphorus pentoxide is, as demonstrated by the experiment, a snowlike, amorphous substance. It is fusible at red heat and is readily volatilized. When plunged into water it hisses, like a red-hot iron, but does not at once entirely dissolve, as a few flakes of metaphosphoric acid, HPO_3 , always remain suspended in the liquid for some time. Its great feature is its attraction for water; left exposed to the air for a few minutes only, it deliquesces entirely, becoming converted into phosphoric acid. It is often used in laboratories as a dehydrating agent, and will even remove water from oil of vitriol. It has no action on dry blue litmus paper.

58. Phosphoric acid, frequently called *orthophosphoric acid* to distinguish it from metaphosphoric, is obtained by the action of boiling water on phosphorus pentoxide. Its formula is H_3PO_4 , and its molecular weight is 98.06.



A method commonly employed for the preparation of phosphoric acid consists of oxidizing phosphorus with nitric acid, when the following reaction occurs:



This solution, on evaporation at the close of the reaction, yields a viscid liquid from which colorless crystals of phosphoric acid may be obtained.

EXPERIMENT.—Pour into a beaker about 6 inches high 30 cubic centimeters of concentrated nitric acid and 15 cubic centimeters of water; drop a few small pieces of phosphorus into the diluted acid, and heat the whole gently. Nitrous fumes are evolved, and the phosphorus is dissolved. Should the action cease before the whole of the phosphorus has disappeared, add a little more acid. At the close of the reaction, evaporate the liquid until it attains a temperature of 150° C. Phosphoric acid remains.

Commercially, the acid, which, however, is somewhat impure, is prepared by treating bone ash (calcium phosphate) with sulphuric acid.

59. Phosphoric acid thus prepared is a sirupy liquid, which by evaporation gives hard, transparent, prismatic crystals that deliquesce in the air. The solution is intensely acid and is odorless. From ammoniacal solutions of magnesium sulphate, it precipitates magnesium ammonium phosphate—a white, crystalline compound—sometimes called *triple phosphate*. With silver nitrate, phosphoric acid, when neutralized by ammonia, gives yellow silver phosphate. On heating the aqueous solution of phosphoric acid to 213° C., pyrophosphoric acid is obtained, and on raising the temperature still higher, meta-phosphoric acid. Phosphoric acid contains 3 atoms of replaceable hydrogen, and is consequently tribasic; it is therefore capable of forming acid, normal, and double salts. In the normal salts the 3 atoms of hydrogen is replaced by metals; but in the acid salts either 1 or 2 atoms of hydrogen may remain. The following series is illustrative of the various salts of phosphoric acid:

ACID SALTS

Primary sodium phosphate, H_2NaPO_4
Secondary sodium phosphate, HNa_2PO_4
Acid calcium phosphate, $HCaPO_4$

NORMAL SALTS

Potassium phosphate, K_3PO_4
Barium phosphate, $Ba_3(PO_4)_2$
Bismuth phosphate, $BiPO_4$

DOUBLE SALTS

Ammonium magnesium phosphate, NH_4MgPO_4
Potassium barium phosphate, $KBaPO_4$

The acid and normal salts are called primary, secondary, or tertiary salts, according as 1, 2, or 3 hydrogen atoms is replaced to form them.

60. Metaphosphoric Acid.—In 1833, Graham showed that phosphoric acid loses water on being strongly heated, and

that, on cooling, it becomes a transparent icelike solid, which he named *glacial phosphoric acid*:



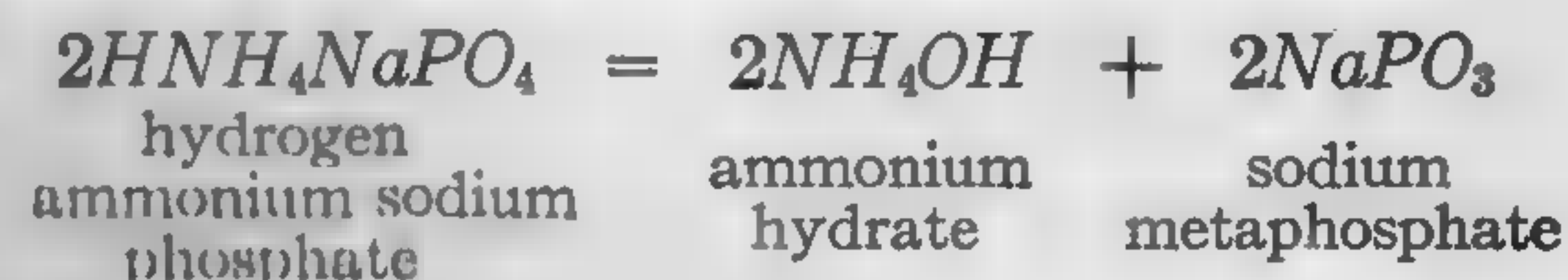
This acid is also prepared by dissolving phosphorus pentoxide in cold water:



Metaphosphates are produced by igniting primary phosphates:



or phosphates that have 2 atoms of volatile base:



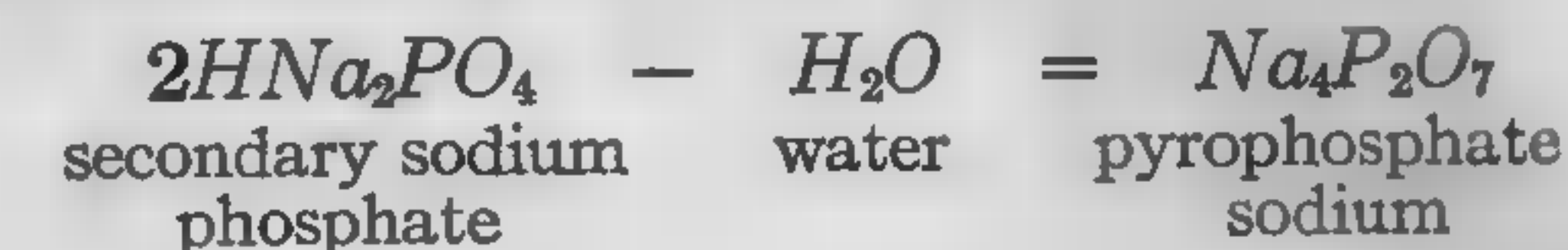
Metaphosphoric acid is obtained by decomposing metaphosphates. Its formula is HPO_3 , and its molecular weight is 80.048.

Metaphosphoric acid is a transparent, colorless, hard, glassy mass that, though very soluble in water, is not crystallizable. Dissolved in water, it forms a strongly acid solution that gradually takes water from the air and forms orthophosphoric acid; this transformation is hastened by boiling. It possesses the property of coagulating albumin—a property that phosphoric acid does not possess—and gives a white precipitate with silver nitrate. Being monobasic, it forms but one class of salts. When the aqueous solutions of these salts are boiled they are converted into primary orthophosphates. It is distinguished by a remarkable tendency to produce polymeric forms, called di-, tri-, tetra-, and hexa-metaphosphates, respectively.

61. Pyrophosphoric, or Diphosphoric, Acid.—In 1820, Clark discovered a variety of phosphoric acid intermediate between the two forms described (produced by heating a solution of orthophosphoric acid to 240°C .); this he named pyrophosphoric acid. Two molecules of the orthophosphoric acid together lose 1 of water:



Pyrophosphates, sometimes known as *diphosphates*, are produced by igniting a phosphate that has 1 atom of hydrogen.



Pyrophosphoric acid generally occurs in solution, but may be obtained by evaporation at 213°C . as a soft glass or in semi-crystalline masses. Its solution is strongly acid, does not coagulate albumin, and gives a white precipitate with silver nitrate. Being tetrabasic, pyrophosphoric acid forms a large series of acid, normal, and double salts. Its formula is $H_4P_2O_7$, and its molecular weight 178.11.

On boiling its solution, pyrophosphoric acid takes up a molecule of water and becomes orthophosphoric acid; on igniting, it loses 1 molecule of water, becoming metaphosphoric acid.

62. Other Acids of Phosphorus.—Two other acids of pentad phosphorus are **phosphorous** and **hypophosphorous**

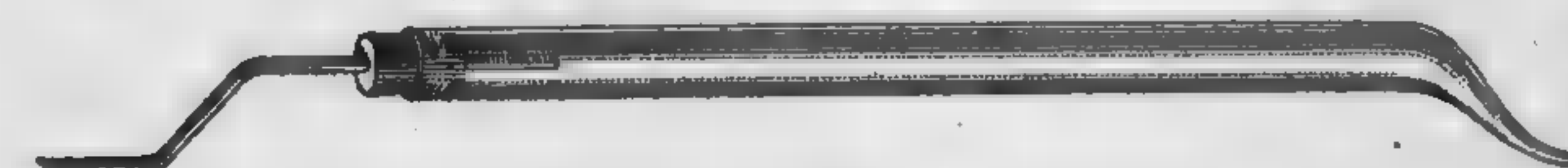


FIG. 10

acids. Phosphorous acid has the formula H_3PO_3 , is dibasic, and forms so-called phosphites. Hypophosphorous acid has the formula H_3PO_2 , is monobasic, and is obtained by decomposing barium hypophosphite with sulphuric acid. Hypophosphites are formed by boiling phosphorus in alkaline solutions.

63. Phosphorus trioxide, or phosphorous anhydride, P_2O_3 , is formed by heating phosphorus in a limited supply of air, as by putting a piece of phosphorus in the glass tube, such as shown in Fig. 10, drawing air through the tube, and warming the tubes gently. In this way not enough air can get access to the phosphorus to form the pentoxide. It is thus obtained as a waxlike mass. It may also be condensed in the form of feathery crystals. Phosphorus trioxide has an unpleasant garlic-like odor, melts at 22.5°C . and boils at 173°C . When pure it is unaltered by light, but when impure it changes to a dark-red color, due to the separation of red phosphorus. On

exposure to the air the trioxide burns, forming the pentoxide. The trioxide is readily converted into phosphorous acid by water.

Other oxides of phosphorus have been prepared, but as they are of no importance and little is known of them, they will not be treated here.

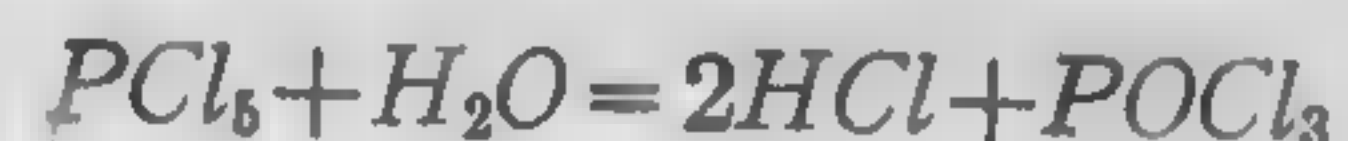
HALOGEN COMPOUNDS OF PHOSPHORUS

64. Phosphorus unites with the halogens to form compounds of the types PX_3 and PX_5 ; the most important are the chlorides.

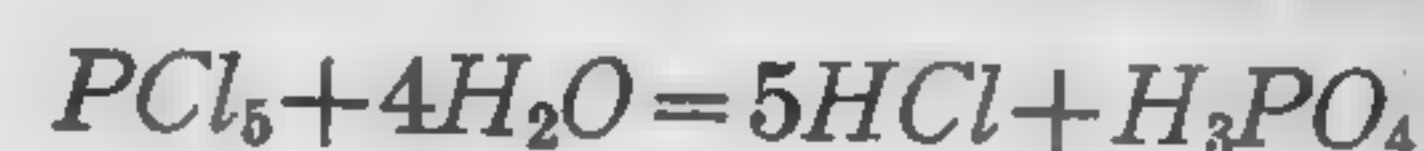
Phosphorus trichloride, PCl_3 , is a volatile liquid with a very pungent smell, formed by direct union of the elements. The product at first formed contains some pentachloride, which is removed by distilling with phosphorus. Water decomposes phosphorus trichloride, yielding hydrochloric acid and phosphorous acid:



By acting on phosphorus trichloride with chlorine, *phosphorus pentachloride*, PCl_5 , is formed. This is a solid that fumes strongly in moist air. By the addition of a little water it yields hydrochloric acid and *phosphorus oxychloride*, $POCl_3$;



with more water it yields hydrochloric acid and phosphoric acid:



65. **Summary.**—Phosphorus does not occur uncombined in nature, but abundantly as a constituent of various rocks. It is obtained from phosphates by reduction with carbon, is inflammable, and exists in two forms that differ widely from each other in properties.

Phosphine is prepared by heating phosphorus with potassium-hydrate solution, and is a gas with the odor of putrid fish. It usually ignites spontaneously owing to impurities.

Phosphoric acid is formed either by the action of boiling water on phosphorus pentoxide or by the oxidation of phosphorus by nitric acid. This acid is tribasic, and forms an extended series of salts.

66. **Laboratory Directions.**—The student is sufficiently familiar with the properties of phosphorus to know that it requires extremely careful handling. Never touch it with the fingers; always use a pair of forceps. Do not keep it out of water, and when a piece is to be cut from a stick, place it in a basin and cut under water. In experiments where carbon disulphide is used, be careful that the main supply bottle is kept at a distance from the phosphorus.

At times, in the experiment in Art. 48, the phosphorus reignites on the top of the tube on the removal of the stopper; should it do this, stopper the tube again and keep for a day or two longer. Or, if wished, a current of carbon dioxide may be passed down the tube, until the whole of the phosphorus vapor is displaced. The carbon disulphide may then be poured in safely.

In the preparation of phosphine (see the experiment in Art. 52), the coal gas is passed in, in order to expel any air, as otherwise the phosphine would take fire within the flask and possibly burst it. Remember that if any air remains with the coal gas, the phosphine may explode the mixture, and so cause considerable damage by scattering the molten phosphorus. This experiment is given more for the purpose of serving as an illustration than with the expectation that the inexperienced student is going to perform it. Should, however, the student desire to perform it, it would, according to the instructor's opinion, be safer to displace the air with carbon dioxide than with coal gas. At the close of the experiment, allow the liquid in the flask to cool until water is drawn into it from the trough. Pull out the stopper, holding the flask in an old cloth, as the gas within the flask will take fire; have in readiness, therefore, a vessel of cold water, with which at once fill the flask to the brim.

ARSENIC

Symbol As. Atomic weight 74.96. Density 149.92. Valence III and V. Molecular weight 299.84.

67. History and Occurrence.—While arsenic is a perfect analogue of phosphorus it at the same time possesses a metallic luster and conducts electricity. It does not, however, form a base with oxygen. In its free state it is very similar to the metals. Sulphides and the oxides of arsenic have been known for many years. Brandt in 1773 was the first to carefully examine arsenic and to give it its place among the non-metals.

Arsenic occurs widely distributed both native and in combination with metals. Most sulphides of zinc and iron contain arsenic, hence it is very frequently found in these metals and in sulphuric acid made from the sulphide ores of these metals. Arsenic occurs most frequently as the sulphides, realgar, As_2S_2 , and orpiment, As_2S_3 , also as mispickel, $FeS_2 \cdot FeAs_2$, arsenical iron and nickel, $FeAs_2$, $NiAs$, smaltite, $CoAs_2$, and proustite, $3Ag_2S \cdot As_2S_3$. Arsenic is obtained in considerable quantities in the form of arsenious oxide as a by-product in the working of gold, silver, and lead ores.

68. Preparation and Properties.—Arsenic is obtained from arsenical pyrites, or mispickel, by heating it in earthen retorts; the arsenic, being volatile, sublimes and condenses in the cooler portions of the retort, toward its mouth. In certain districts, arsenic is obtained by reducing its oxide with charcoal—a method by which it is obtained in a much purer form.

Where arsenic is obtained as a by-product in the reduction of gold, silver, and lead ores, the dust carried from the furnaces with the draft deposits the arsenic in long woolen bags. From these bags it is charged into mechanical roasters, which sublime the arsenic and it is then condensed in long brick chambers. The impure arsenious oxide thus obtained is resublimed, when it becomes an almost absolutely pure product.

Arsenic presents the appearance of a dark, steel-gray, brittle solid, possessing a distinctly metallic luster, and having a specific gravity of 5.6 to 5.9. It occurs in two allotropic modifications, as, besides the steel-gray variety, which crystallizes in rhombohedrons, and possesses the above-mentioned specific gravity, an amorphous, black, vitreous variety, of specific gravity 4.71, exists, which at 360° C. passes into the crystalline variety with considerable evolution of heat. Arsenic is volatile in closed vessels at 500° C.; its vapor is yellow and possesses a peculiar odor, which resembles that of garlic. In the air, it gradually oxidizes at ordinary temperatures, and at a red heat it burns with a bluish-white flame, producing arsenic trioxide. Arsenic and all its compounds are active poisons.

ARSENIC AND HYDROGEN

69. Arsine, formerly called *arseniureted hydrogen*, is the only compound of arsenic and hydrogen whose existence has been satisfactorily established. It was discovered by Scheele in 1775. Its formula is AsH_3 , and its molecular weight 77.984. Arsine is formed by the action of hydrochloric or sulphuric acid on zinc arsenide, thus:



It is also formed by the action of nascent hydrogen on solutions of arsenic.

Great care must be taken in the preparation of arsine, as it is extremely poisonous.

Arsine is a poisonous, colorless gas with a strong garlic-like odor, and has a specific gravity of 2.7. It may be liquefied at -40° C. and solidified at -113° C. It is soluble in five times its volume of water. It takes fire readily in the air, burning with a bluish-white flame and evolving white fumes of arsenic trioxide. If a cold surface of porcelain is held in this flame, metallic arsenic is deposited on it as a dark stain, or *tache*. Arsine is readily decomposed when the tube through which it is passing is heated to redness, a dark mirror-like ring of metallic arsenic being formed just beyond the heated spot.

The gas is also decomposed when passed into a solution of silver nitrate, forming arsenious acid and precipitating metallic silver. When hydrogen is evolved from any liquid containing arsenic, traces of arsine are always formed; it can be detected by the smell or by the previously mentioned tests, which are so delicate that .001 milligram of arsenic can be detected.

EXPERIMENT.—The importance of arsine lies in its application for the detection of arsenic in what is known as *Marsh's test*, which depends on the production of arsine whenever arsenic is in a solution in which nascent hydrogen is formed.

A convenient form of Marsh's apparatus is shown in Fig. 11. It consists of a three-necked Woulff's bottle *A*, through the middle tubulure of which a funnel *B* passes for the supply of liquid, while one of the side openings has

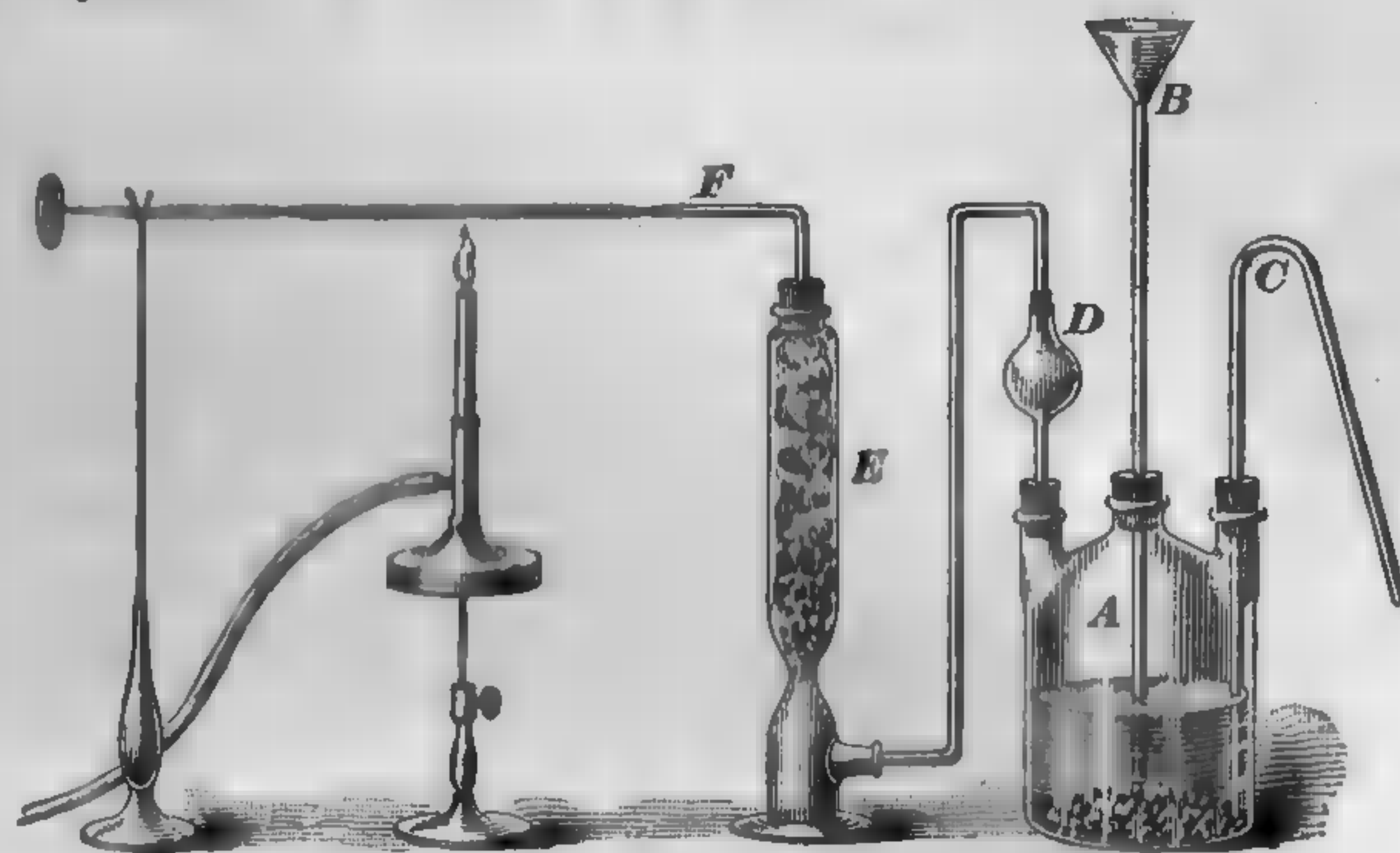


FIG. 11

a siphon tube *C* for withdrawing the exhausted acid, and the other tubulure has a delivery tube with a bulb *D*. This bulb is filled with cotton, to retain any impurities that might be mechanically carried over by the gas. Attached to this leading tube is a jar *E* filled with potassium hydroxide and calcium chloride; the object of this mixture is to purify the evolved gas, which then passes through another leading tube *F*, made of hard glass and drawn at intervals, as shown in the cut.

Small pieces of pure zinc are first placed in the Woulff's bottle, to which is added pure sulphuric acid, previously diluted with 3 parts of distilled water and thoroughly cooled (so as to have normal temperature). After allowing sufficient time for the air to be expelled from the apparatus, the leading tube *F* is heated to dull redness by a Bunsen burner. If no dark deposit appears beyond the flame in 15 minutes, the materials employed may be considered free from arsenic. The liquid suspected to contain arsenic is then added through the funnel tube. If arsenic should be present, the flame of hydrogen burning at the end of the tube will, often

in a few seconds, change its color, becoming whitish, and will deposit a dark-brown metallic spot on a porcelain plate pressed against it. If the tube is again heated, the arsine will be decomposed, and the arsenic be deposited as a dark metallic ring. According to Wormley, $\frac{1}{10000}$ grain of arsenic trioxide in 100 grains of the solution may be detected by this test.

It should never be forgotten that arsine is one of the most active poisons known. *Experiments made with it should, therefore, be made only with the very greatest care.*

OXIDES AND ACIDS OF ARSENIC

70. The oxides of arsenic, with their corresponding acids, are:

OXIDES	ACIDS
Arsenic trioxide, As_2O_3	Arsenious acid, H_3AsO_3
Arsenic pentoxide, As_2O_5	Arsenic acid, H_3AsO_4

71. Arsenic trioxide, As_2O_3 , or *arsenious anhydride*, has long been known under the names of *white arsenic* and *arsenious acid*. It is prepared by the roasting of ores containing arsenic, the vapors given off being condensed in long brick chambers, where they condense in the form of a white powder. It is purified by again subliming and recondensing.

72. Arsenic trioxide, sometimes called *arsenious oxide*, occurs in two distinct modifications. When the arsenic-trioxide vapor is condensed at a temperature of $400^\circ C.$, it forms a transparent vitreous mass of a specific gravity of 3.738, which, when deposited slowly at a slightly lower temperature, crystallizes in right rhombic prisms. The second variety is obtained either by condensing the vapor at $200^\circ C.$, or by cooling a saturated aqueous solution of arsenic trioxide of the first modification, as brilliant transparent octahedral crystals of specific gravity 3.689. The vitreous modification passes gradually at ordinary temperatures, rapidly at about $100^\circ C.$, into the second variety, forming a white, opaque mass resembling porcelain, commonly known as *white arsenic*.

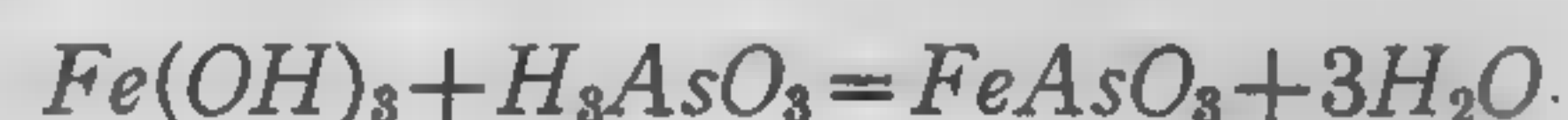
When the vitreous modification is dissolved to saturation in hot hydrochloric acid and left to cool slowly, it crystallizes

in octahedrons, the formation of each crystal being accompanied by a flash of light.

Arsenic trioxide volatilizes at 218° C. yielding a vapor that has a density of about 198 instead of about 99, a fact that indicates that the vitreous modification, which is formed at high temperatures, has the molecular formula As_4O_6 . Both varieties are sparingly soluble in water, but are more soluble in hydrochloric acid and in alkaline solutions.

Arsenic trioxide is frequently mistaken for flour, but it may be easily recognized by its weight and by sprinkling it on red-hot coal, when a strong odor of garlic is obtained.

Arsenic trioxide is only slightly soluble in water. The solution has a sweet, unpleasant metallic taste, is feebly acid, and is very poisonous. The best antidote for arsenic in any form is freshly precipitated ferric hydroxide. Workers in arsenic plants usually apply an ointment of ferric hydroxide and lanoline to their faces previous to beginning work. The ferric hydroxide is best precipitated by means of magnesium hydroxide. Ferric hydroxide forms an insoluble arsenite with the arsenic and thus prevents further absorption of the poison. The reaction of ferric hydroxide and arsenic is represented by the following quotation:



73. Arsenious acid, H_3AsO_3 , is obtained when arsenic trioxide is dissolved in water. It has never been prepared in a pure state, as the solution probably is really a solution of the trioxide. This solution has a slight acid reaction and forms salts (*arsenites*). By exactly neutralizing the solution with ammonia and adding silver nitrate, a salt is obtained corresponding to the formula Ag_3AsO_3 , which shows the acid to be tribasic.

Several series of arsenites are known, namely, ortho-arsenites, meta-arsenites, and pyro-arsenites.

The alkali arsenites are soluble in water, absorb oxygen from the air, showing they are powerful reducing agents, they themselves being converted into arsenates. The alkali arsenites are frequently used in sheep dips and in sprays, and a soap

containing these salts, together with other ingredients is sometimes used to preserve the skins of animals.

When arsenious oxide is dissolved in a solution of potassium carbonate and a solution of copper sulphate is added an arsenite of copper is precipitated. This precipitate, known as *Scheele's green*, $CuHAsO_3$, is a very poisonous coloring matter that is sometimes used in the manufacture of wall paper. As this coloring matter can be fixed only with glue or paste it rubs off the paper in a fine dust and is diffused through the air of the room and a small quantity is inhaled by the occupants of the room with each breath.

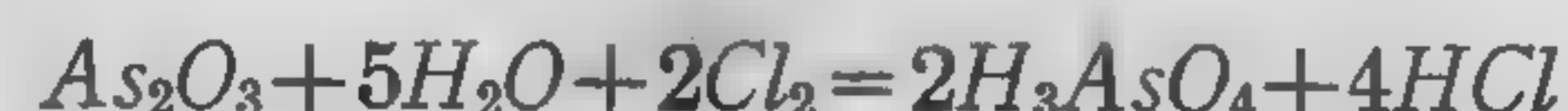
The presence of arsenic in a wall paper may be detected as follows: A sample of the paper is soaked for some time in ammonium hydroxide, which dissolves the copper arsenite. This solution is then tested by *Reinch's* test for arsenic by acidifying with hydrochloric acid, which should compose at least one-tenth of the volume of the solution, and boiling with a strip of bright copper, the arsenic being deposited on the copper as a gray film. To further identify the deposit, wash the copper with distilled water, dry, and heat in a glass tube, to obtain the arsenic mirror or the crystalline structure. All the reagents used must be tested for arsenic in the same manner to be perfectly sure that the arsenic is in the wall paper.

Other well-known arsenites are *Paris green* or *Schweinfurt green*, which is a copper aceto-arsenite made by mixing equal parts of hot solutions of arsenic trioxide and copper acetate, and *Fowler's solution*, which is prepared by dissolving arsenious acid in a solution containing an equal weight of potassium bicarbonate.

74. Arsenic pentoxide, As_2O_5 , is obtained as a white porous mass when arsenic trioxide is heated in the presence of an oxidizing agent to a temperature slightly below a red heat. Although arsenic resembles phosphorus very closely, it differs from the latter in that when burned in air or oxygen it oxidizes to the trioxide only. Arsenic pentoxide can be prepared directly from arsenic acid by heating it to a dull redness. Arsenic pentoxide has a specific gravity of 3.73, is slowly soluble

in water, and deliquesces in moist air, forming arsenic acid. Heated to a bright red heat it decomposes into oxygen and arsenic trioxide, and heated with reducing agents it is easily reduced to free arsenic.

75. Arsenic acid, H_3AsO_4 , was first prepared by Scheele in 1775 by the oxidation of arsenic trioxide with nitric acid. He also prepared it by the action of moist chlorine gas on the trioxide, thus:



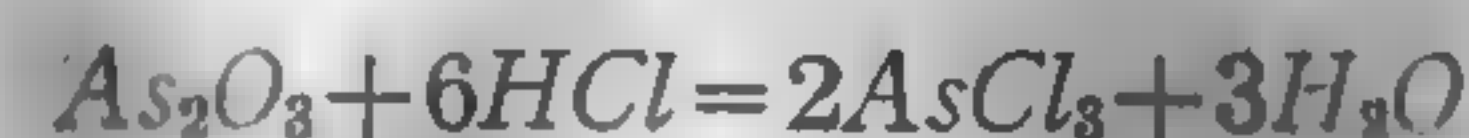
On evaporation, long rhomboidal crystals containing a small quantity of water of crystallization separate. These crystals deliquesce in the air, and when heated to $100^\circ C.$, lose their water of crystallization and yield ortho-arsenic acid, H_3AsO_4 . This acid possesses a very acid, unpleasant metallic taste, and is almost as poisonous as the trioxide. On heating the ortho-arsenic acid to $180^\circ C.$ it loses water, and hard, glittering crystals of pyro-arsenic acid, $H_4As_2O_7$, are obtained. Between $200^\circ C.$ and $204^\circ C.$, another molecule of water is expelled and a white crystalline mass of meta-arsenic acid is left. On the addition of water, the last two acids are reconverted into ortho-arsenic acid.

Ortho-arsenic acid is readily soluble in water, is tribasic, and forms salts, the *arsenates*, isomorphous with the phosphates. It is used in calico printing as a substitute for tartaric acid, and in the manufacture of the beautiful dye known as *magenta*.

ARSENIC AND CHLORINE

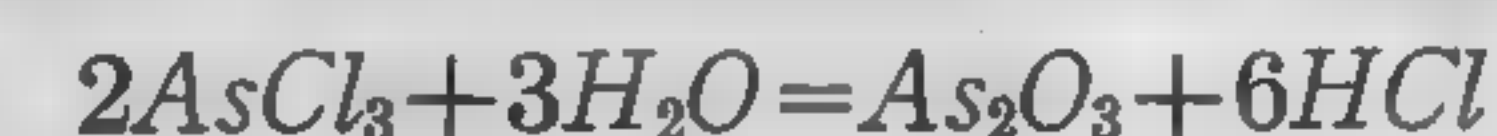
76. The compounds of arsenic with the halogens are analogous with the corresponding phosphorus compounds. They are the result of the direct union of their constituents. The slight metallic character of arsenic is shown in the chloride which may be formed by the action of hydrochloric acid on the oxide.

77. Arsenic trichloride, $AsCl_3$, is prepared by distilling arsenic trioxide with strong hydrochloric acid:



It can be prepared also by passing dry chlorine over heated arsenic. As the product obtained by this method always contains an excess of chlorine, it is purified by passing it over more heated arsenic.

Arsenic trichloride is a colorless, oily liquid with a specific gravity of 2.21. It boils at $130^\circ C.$, evolving a heavy, colorless vapor, and solidifies in long, pearly needles at $-18^\circ C.$ It evaporates in the air, giving off dense white fumes, and is extremely poisonous. A small quantity of water dissolves arsenic trichloride without change, but considerable water decomposes it into hydrochloric acid and arsenic trioxide, thus:



78. Arsenic tribromide, $AsBr_3$, and *arsenic tri-iodide, AsI_3 ,* are prepared in the same manner as the trichloride. The tribromide forms colorless, deliquescent crystals that melt at $20^\circ C.$ and boil at $220^\circ C.$ It has a strong odor of arsenic, and is acted on by water in the same way as the trichloride. Arsenic tri-iodide forms bright-red, hexagonal crystals, of a specific gravity of 4.4, and that melt at $146^\circ C.$

79. Arsenic forms two fluorides, the **trifluoride, AsF_3 ,** and the **pentafluoride, AsF_5 .** The former is prepared by distilling arsenic trioxide with fluorspar and sulphuric acid. The fluoride is a transparent, colorless liquid that fumes strongly in the air; it has a powerful, pungent odor, solidifies at $-8.5^\circ C.$, boils at $61^\circ C.$, and is decomposed by water. The pentafluoride is formed by distilling a mixture of arsenic trifluoride, antimony pentafluoride, and bromine. It is a colorless gas that liquifies at $-53^\circ C.$ and becomes solid at $-80^\circ C.$

ARSENIC AND SULPHUR

80. Six sulphides of arsenic are known: Three arsenic subsulphides, As_3S , As_4S , and As_5S ; arsenic disulphide, or realgar, As_2S_2 ; arsenic trisulphide, or orpiment, As_2S_3 ; and arsenic pentasulphide, As_2S_5 .

81. Arsenic disulphide, As_2S_2 , occurs in nature in the form of transparent red crystals that belong to the type of the

oblique rhombic prism. It is formed artificially by heating arsenic acid with the proper proportion of sulphur. It is fusible and may be crystallized by slow cooling. When strongly heated in a closed vessel, it boils and distils without alteration; but, when heated in the air, it burns into arsenic trioxide and sulphur dioxide. The alkaline sulphides and ammonium sulphide dissolve realgar, leaving a brown powder that is considered a subsulphide of arsenic. A boiling solution of potassium hydrate also dissolves realgar, forming a mixture of potassium arsenite and sulpharsenite; the latter is a soluble compound of arsenic trisulphide and potassium sulphide.

82. Arsenic trisulphide, or orpiment, As_2S_3 , is found in nature in yellow prismatic crystals. It may be obtained by fusing together arsenic and sulphur in the proper proportion, or arsenic trioxide and sulphur; in the latter case, sulphur dioxide is disengaged and arsenic trisulphide sublimes. Thus prepared, orpiment occurs as crystalline masses of a yellow, or, more correctly, yellow-orange color, and is of a pearly aspect. It is fusible and volatile, burning with a pale-blue flame.

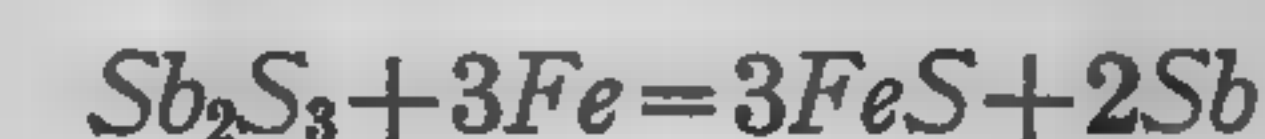
83. Arsenic pentasulphide, As_2S_5 , is precipitated when an excess of hydrogen sulphide is passed into a solution of arsenic acid heated to 70°C . It is a lemon-yellow powder that is insoluble in water and may be fused and distilled without alteration.

ANTIMONY

Symbol Sb. Atomic weight 120.2. Valence III and V.

84. History and Occurrence.—Antimony has been known for many hundred years; it was prepared in the pure state by Basil Valentine toward the end of the 15th century. It occurs in nature both free and in combination. Its most abundant source is the sulphide known as *stibnite*, but it also exists in combination with oxygen in the minerals *valentinite*, *senarmontite*, and *cervantite*, with silver in *dycrasite*; and with silver and sulphur in *pyrargyrite* and *miargyrite*.

85. Preparation and Properties.—Antimony is obtained from its sulphide, Sb_2S_3 , by heating it in covered pots with metallic iron:



The excess of iron is removed by heating with charcoal and fluxes, such as sodium carbonate, and a further addition of the sulphide. The metal extracted in this way is contaminated with arsenic, iron, sulphur, and often lead or copper. It may be further purified by remelting with potassium hydroxide when, on solidifying, it shows fernlike markings due to crystallization, and is known as *star metal*.

It is prepared also by roasting the sulphide, when the sulphur burns and antimony trioxide is formed. The oxide is then reduced with carbon.

Antimony is a brilliant, bluish-white, brittle element, of specific gravity 6.715. It crystallizes in rhombohedrons, thus being isomorphous with arsenic and red phosphorus. It melts at 430°C ., and at a white heat may be distilled. It scarcely tarnishes in the air, but takes fire at a red heat, producing antimony trioxide. It is strongly attacked by chlorine, forming antimony trichloride, $SbCl_3$, and pentachloride, $SbCl_5$. Antimony is so brittle that its only use in the free state is for the construction of thermoelectric piles. It is used in several useful alloys, however, as, for example, in type metal, Britannia metal, pewter, in pharmacy, and in calico dyeing and printing.

ANTIMONY AND HYDROGEN

86. Stibine.—Antimony and hydrogen form a compound known as stibine, SbH_3 , which is similar to the hydrogen compounds of nitrogen, phosphorus, and arsenic in constitution, but it resembles arsine very closely. Stibine is a colorless, peculiarly disagreeable smelling, poisonous gas. It can be condensed to a colorless liquid that boils at -17°C . and solidifies at about -85°C . It is slightly soluble in water, and is very easily ignited, burning with a greenish-white flame and giving off white fumes of the trioxide.

Whenever an antimony compound is present in a solution from which hydrogen is being evolved, a gas escapes, mixed with the hydrogen, causing it to burn with a bluish-white flame. This gas is stibine, which is decomposed by heat, like arsine, but the metallic deposit of antimony is easily distinguished from that of arsenic by being less volatile, by its darker color, its smoky appearance, its insolubility in hypochlorites, and its solubility in ammonium sulphide.

OXIDES AND ACIDS OF ANTIMONY

87. The three oxides and three acids of antimony known are:

OXIDES	ACIDS
Antimony trioxide, Sb_2O_3	Orthoantimonic acid, H_3SbO_4
Antimony tetroxide, Sb_2O_4	Metantimonic acid, $HSbO_3$
Antimony pentoxide, Sb_2O_5	Pyroantimonic acid, $H_4Sb_2O_7$

88. Antimony trioxide, Sb_2O_3 , occurs in nature as valentinite, or white ore of antimony. It is the product of the combustion of antimony in air or of its oxidation by nitric acid. The trioxide formed by burning antimony in air always contains some tetroxide, and by heating it long enough, at a sufficiently high temperature, it is completely converted into the tetroxide. Toward some of the stronger bases, like sodium hydrate, the trioxide acts as an acidic oxide. Toward most bases, however, it does not show acid properties, and toward the stronger acids it acts as a base. Oxidizing agents convert it into antimonic acid.

89. Antimony tetroxide, Sb_2O_4 , as previously stated, may be prepared by igniting the trioxide in the air. It occurs native as antimony ochre. It can be obtained more readily by igniting antimonic acid, H_3SbO_4 , thus driving off water and oxygen. At ordinary temperatures the tetroxide is white, but becomes yellow when heated. It has the properties of an acidic oxide toward strong bases, but toward strong acids it acts as a weak base.

90. Antimony pentoxide, Sb_2O_5 , is prepared by gently igniting antimonic acid to expel water, but care must be taken not to heat it high enough to expel oxygen. It cannot be formed by the addition of oxygen to the tetroxide, but if ignited, easily breaks up into the tetroxide and oxygen. It conducts itself as an acidic oxide.

91. Acids of Antimony.—Antimonic acid, H_3SbO_4 , is the final oxidation product, when antimony is treated with aqua regia. It may also be obtained by treating one of its salts with sulphuric acid. It is similar to phosphoric and arsenic acids and occurs in three forms. The ortho acid, H_3SbO_4 , is formed when antimony pentachloride is decomposed with water. When dried at 100°C ., the pyro acid, $H_4Sb_2O_7$, is formed, and when heated to 200°C . the meta acid, $HSbO_3$, results. The ortho and meta acids are white amorphous bodies soluble in potassium hydrate and only slightly soluble in water. The pyro acid, while only sparingly soluble in water is more soluble than is the meta; the normal fixed alkali salts of the pyro acid are soluble in water, and when heated to 200°C . the pyro acid is converted in the meta acid.

ANTIMONY AND CHLORINE

92. Antimony trichloride, $SbCl_3$, may be prepared by treating antimony directly with chlorine, or by dissolving antimony in hydrochloric acid with the addition of nitric acid and distilling the product. This compound is a solid crystalline substance that is quite soft, and on account of its consistency is called *butter of antimony*. It melts at 73°C ., boils at 223°C ., and deliquesces in the air. When treated with water an oxychloride is formed, the composition of which depends more or less on the temperature of the water.

93. Antimony pentachloride, $SbCl_5$, may be obtained by treating the trichloride with an excess of chlorine. It is similar to phosphorus pentachloride, but is more readily converted into the trichloride according to the equation:



This is similar to the action of the pentoxide of phosphorus in breaking down into the trioxide and oxygen. When the pentachloride is acted on by water it at first yields an oxychloride, but by further action it yields antimonious acid, H_3SbO_4 .

ANTIMONY AND SULPHUR

94. Antimony trisulphide, Sb_2S_3 , occurs in nature as the mineral stibnite, and is the chief ore of antimony. It may be prepared by treating a solution of antimony trichloride with hydrogen sulphide, when the trisulphide separates as an orange-colored precipitate. The naturally occurring trisulphide is either gray or black. The trisulphide dissolves in solutions of metallic sulphides, forming salts of sulphantimonious acid.

95. Antimony pentasulphide, Sb_2S_5 , is prepared by passing hydrogen sulphide into antimonious acid, or by decomposing a sulphantimonate by means of a strong acid. When dry it is a golden-yellow powder that readily dissolves in solutions of metallic sulphides, forming sulphantimonates.

BISMUTH

Atomic weight 208.0. Symbol *Bi*. Valence III and V.

96. History and Occurrence.—Bismuth was first distinctly recognized by Basil Valentine in the 15th century. Agricola, in 1529, called it *bismetum*, and Paracelsus mentions it as *wismeat*. It was for a long time confounded with other elements, especially with lead, tin, and antimony. Pott, in 1739, first described its characteristic actions. This element occurs in the native condition in veins traversing gneiss, clay slate, and other crystalline rocks. It also occurs as oxide, forming the mineral *bismite*; as sulphide, or *bismuthinite*; as sulphotelluride, or *tetradymite*; and as carbonate, or *bismutite*.

97. Preparation and Properties.—Bismuth for use in the arts is obtained on a large scale from the native bismuth

by placing this, mixed with the rocky gangue, in iron tubes slightly inclined, which are heated in a furnace. The bismuth melts and flows out at the lower ends of the tubes into suitable vessels, from which it is ladled into molds. The bismuth of commerce is mostly contaminated with arsenic, iron, and various other metals, from which it may be freed by fusion with potassium nitrate. Chemically pure bismuth may be obtained by reducing bismuth nitrate, $Bi(NO_3)_3$, with charcoal.

Bismuth is a hard, brittle, brilliant metal of a reddish-white color. It has a great tendency to crystallize on fusion; by melting a considerable quantity of it, allowing it to cool until a crust forms on the surface, piercing this and pouring out the portion that still remains liquid, crystals of great size and beauty may be obtained. Owing to a slight superficial oxidation, these crystals, as usually obtained, are beautifully iridescent. Bismuth has a specific gravity of 9.747; it melts at $264^\circ C.$, and expands one thirty-second of its bulk on solidifying. It may be distilled at a white heat. It is unaltered in dry air, but is tarnished in the presence of moisture. Strongly heated, it takes fire, burning with a bluish-white flame, and forming bismuth trioxide, Bi_2O_3 . Chlorine and nitric acid attack it readily, but hydrochloric and sulphuric acids, when cold, have no action upon it.

Bismuth is used in the arts chiefly for forming alloys. *Rose's fusible metal* is composed of 1 part of lead, 1 of tin, and 2 of bismuth; it melts at $94^\circ C.$ *Lipowitz's fusible metal* contains 3 parts of cadmium, 4 of tin, 8 of lead, and 15 of bismuth; it melts at $60^\circ C.$ An alloy of lead and bismuth is used in the so-called *permanent metallic pencils*. Bismuth is also employed in medicine.

OXIDES AND ACIDS OF BISMUTH

98. There are four oxides of bismuth, and one hydrate that has the form of metarsenic and metantimonous acids, and is generally called *bismuthic acid*. These compounds have basic rather than acidic properties, showing that bismuth should be considered as a base-forming element. Though its metallic characteristics appear to predominate, its general

chemical relations place it in this group. The oxides and acid are as follows:

OXIDES	ACIDS
Bismuth dioxide, Bi_2O_2	Bismuthic acid, $HBiO_3$
Bismuth trioxide, Bi_2O_3	
Bismuth tetroxide, Bi_2O_4	
Bismuth pentoxide, Bi_2O_5	

99. Bismuth dioxide, Bi_2O_2 , may be obtained by adding potassium hydrate to a mixture of bismuth trichloride and stannous chloride. As stannous chloride tends to change to stannic chloride, it acts as a reducing agent, and probably takes some of the chlorine from the bismuth trichloride, forming a compound of the composition $BiCl_2$. The potassium hydrate, acting on this, precipitates bismuth dioxide, Bi_2O_2 , in the form of a brown precipitate. It is obtained also by heating metallic bismuth in the air. It is a citron-yellow powder, stable in the air, and is insoluble in water and in the alkalis.

100. Bismuth trioxide, Bi_2O_3 , is the principal oxide of bismuth and is formed when bismuth is burned in air or oxygen. It may also be prepared by igniting the nitrate, $Bi(NO_3)_3$, at a high temperature. It is a yellow powder, with basic properties. Bismuth tetroxide, Bi_2O_4 , is a reddish-yellow powder of which little is known.

101. When chlorine is led through a concentrated solution of potassium hydrate in which bismuth trioxide is suspended, bismuthic acid, $HBiO_3$, is precipitated; this, when gently heated yields bismuth pentoxide, Bi_2O_5 . Some experimenters claim to have obtained salts of bismuthic acid, such, for example, as $NaBiO_3$, while others have failed. At all events, the acid properties of bismuthic acid, and of the pentoxide, are very weak.

102. Bismuthic acid, $HBiO_3$, as stated above, is obtained by passing chlorine through a concentrated solution of potassium hydrate, in which bismuth trioxide is suspended. It may act as a very weak acid toward strong bases, but its general character is rather basic. It is a beautiful scarlet-red powder which at $120^\circ C.$ gives up its water, forming the pentoxide.

BISMUTH AND CHLORINE

103. Bismuth forms two compounds with chlorine, namely: $BiCl_3$ and $BiCl_2$. The trichloride is the principal one. It may be formed by the direct action of chlorine on bismuth. It is a white, granular, deliquescent substance, fusible at $230^\circ C.$, and volatile at $435^\circ C.$ By contact with water it is decomposed, forming bismuthyl chloride, $BiOCl$, also known as bismuth oxychloride.

The trifluoride, tribromide, and tri-iodide are similarly prepared, and in presence of water these yield precipitates of basic salts.

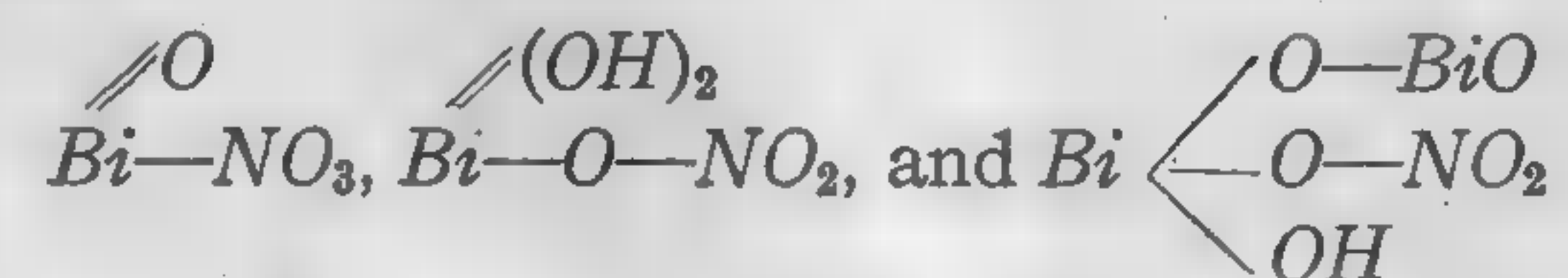
BISMUTH AND SULPHUR

104. Bismuth trisulphide, Bi_2S_3 , occurs in nature as bismuthinite. It is obtained as a black precipitate on adding hydrogen sulphide to solutions of bismuth; but, unlike the sulphides of arsenic and antimony, it is not soluble in solutions of the alkali sulphides. It forms, with metallic sulphides, salts called *sulphobismuthites*, some of which, as that of lead, or *kobellite*, $Pb_3(BiS_3)_2$, and those of copper, called *emplectite*, $Cu(BiS_2)_2$, and *wittichenite*, $Cu_3(BiS_3)_2$, occur in nature.

SALTS OF BISMUTH

105. By treating a solution of bismuth nitrate, $Bi(NO_3)_3$, with a cold solution of potassium hydrate a precipitate of bismuth hydrate, $Bi(OH)_3$, is obtained. If this is dried at $100^\circ C.$ water is driven off, and the hydrate $BiOOH$ results. The salts of bismuth are derived from these two hydrates. The salts derived from the triacid base, $Bi(OH)_3$, are known as *bismuth salts*, and those derived from the monacid base, $BiOOH$, are called *bismuthyl salts*. The most common salts of bismuth are the sulphates and nitrates. By dissolving bismuth trioxide in dilute sulphuric acid, *acid bismuth sulphate*, $BiH(SO_4)_2$, is obtained. This compound is not as stable, however, as *bismuthyl sulphate*, $(BiO)_2SO_4$. Bismuth nitrate, $Bi(NO_3)_3 \cdot 10H_2O$, is obtained by dissolving bismuth

in nitric acid and evaporating to dryness. Water decomposes this salt, forming basic nitrates, the composition of which depends on a number of circumstances, as, for example, the quantity and temperature of the water, the amount of free acid present, etc. Among the best known basic nitrates of bismuth are:



There are many others, however, that are more complex in composition.

INORGANIC CHEMISTRY

(PART 7)

FAMILY 4, GROUP A

GENERAL REMARKS

1. The members of Family 4, Group A, are *carbon, silicon, titanium, zirconium, cerium, and thorium*. The relationship between carbon, the first member of the group, and the other members is not as close as that which exists between the other members. All the members of this group, except titanium, form compounds with hydrogen. In the composition of the hydrogen compounds, carbon and silicon are similar; the other members form compounds having a different composition. These compounds are: CH_4 , SiH_4 , ZrH_4 , CeH_3 , and ThH_3 . Carbon, of course, forms many other compounds with hydrogen, and the power to form homologous series, which is one of the characteristic properties of carbon, is not possessed by the other members of the group. With oxygen all the members of this group form compounds similar in composition to the chief oxide of carbon; they are CO_2 , SiO_2 , TiO_2 , ZrO_2 , CeO_2 , and ThO_2 . The first four are acid, and the last two are basic; hence, in this group, just as in the phosphorus group, there is a gradual gradation of properties, the lighter elements being acid forming, and the heavier ones base forming. The compounds of carbon and silicon are very abundant in nature, those of other members being rare.

CARBON

Symbol *C*. Atomic weight 12.0. Valence II and IV.

2. Occurrence.—Carbon constitutes the most important constituent of all the organic substances. It occurs in the free state in nature in the crystalline forms as *diamond* and *graphite*. When an organic compound is heated with a limited amount of air, a portion of the carbon remains as *amorphous* carbon. Carbon also occurs in peat and lignite and in bituminous and anthracite coal. In combination with hydrogen it



FIG. 1

occurs in mineral oils. It also occurs in the air as carbon dioxide, and in minerals and rocks in the form of a carbonate.

3. Preparation.—By heating wood or coal in a closed vessel, carbon in an impure state may be readily obtained. Water and volatile compounds of carbon with hydrogen and oxygen are driven off; the excess of carbon remains, together with the non-combustible portions of the wood or other body.

EXPERIMENT.—Fit up an apparatus, Fig. 1, consisting of a combustion tube connected by a stopper to a leading tube that terminates in the pneumatic trough, and place some pieces of dry wood in the tube. Fix the tube in the retort stand with its mouth slightly lower than the other

end, in order to prevent any of the liquid that distils from running back on the hot part of the glass tube. Place a bottle for the collection of the gas, and apply heat to the combustion tube; some water and tarry liquid condense in the cooler part of the tube and an inflammable gas passes over into the jar. When the action ceases, a black mass remains of approximately the same shape as the original wood, still retaining the grain and marks of the woody structure. This body is *charcoal*.

This process of heating a body and causing its decomposition, in part, into gaseous and liquid products, which are collected, is termed *destructive distillation*.

4. Properties.—1. *Diamond*.—The form of carbon known as **diamond** is a brilliant, transparent, and, usually colorless solid; sometimes, however, it is colored by impurities; it has a specific gravity of 3.5, and crystallizes in forms belonging to the isometric system, the faces being often rounded, as in Fig. 2. In this form it conducts neither heat nor electricity, but possesses a very high refractive and dispersive power; it is the hardest substance known. Small crystals set in proper

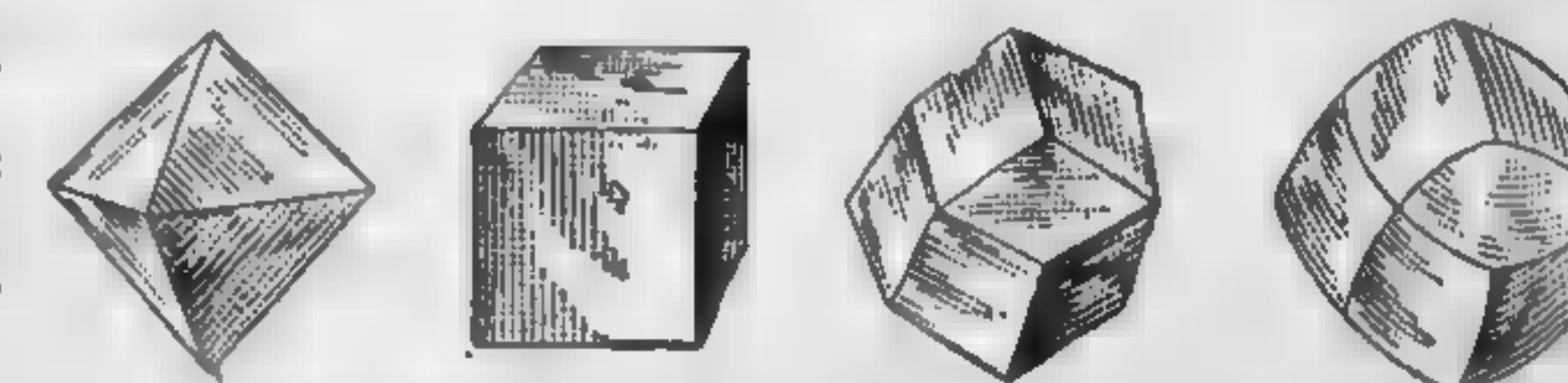


FIG. 2

holders are used for cutting glass. The diamond occurs in India, Borneo, South Africa, and other localities. It is cut for a gem into forms having relations to its direction of cleavage—known as the brilliant, the rose, and the table—by means of diamond dust, which is usually obtained from a dark amorphous diamond (carbonado) found at Bahia, in Brazil. A genuine diamond may be known by its combining the three qualities of extreme hardness—enabling it to scratch hardened steel—high specific gravity, and insolubility in hydrofluoric acid.

Artificial diamonds have been made by dissolving amorphous carbon in molten iron at nearly 3,000° C., and suddenly cooling the metal by pouring it into melted lead. In this way only the surface of the globules of iron is immediately solidified. The interior expands as it cools and creates that pressure on the carbon it contains that appears to be essential to the formation of the diamond. By dissolving the iron in acids,

the diamonds are left. They are, however, of no mercantile value, being only very small fragments; besides they are, so far as brilliancy is concerned, not comparable with the natural product.

If the diamond is exposed to the intense heat of the voltaic arc in a vessel exhausted of air, it becomes converted into a black, cokelike mass, in all its properties closely resembling graphite. Heated in oxygen to about 800° C. it burns to carbon dioxide.

2. *Graphite*.—The second form of carbon, known as **graphite**, differs from the diamond in almost every characteristic. It occurs in compact masses that appear to be more or less crystalline, the more perfect crystals appearing as hexagonal plates, Fig. 3—a crystalline shape that is, as will be seen, totally distinct from that of the diamond. Graphite is a leaden-gray solid with a semimetallic luster, and has consequently received the names *plumbago* and *black lead*. It has a specific gravity of 2 to 2.2, and conducts heat and electricity readily. It is soluble in melted iron, from which it crystallizes on cooling.

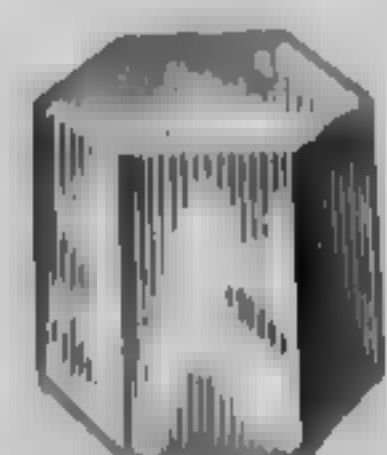


FIG. 3

Graphite occurs, foliated as well as massive, in metamorphic rocks in Siberia, Ceylon, England, Canada, and various places in the United States—as, for instance, in Sturbridge, Mass., Brandon, Vt., Wake, N. C., etc. It is purified by being treated with potassium chlorate and sulphuric acid, and is, after drying, condensed into a solid block by hydrostatic pressure. This purification process is known as *Brodie's process*. The finer qualities of graphite, especially those coming from Siberia, are employed in the manufacture of black-lead pencils; the coarser qualities are used in the manufacture of crucibles, and, as it has a peculiar, greasy feel, it is sometimes used for lessening the friction between two rubbing surfaces of various kinds of machinery. Heated with a mixture of potassium chlorate and nitric acid, graphite is converted into insoluble graphitic acid. Graphite is the only variety of carbon stable at high temperatures. It will, however, burn in oxygen.

3. *Amorphous Carbon*.—This modification of carbon is formed by the carbonization of organic compounds. The

amorphous carbon produced in this manner is named to indicate its origin or method of production. The principal forms are (I) coal, (II) lampblack, (III) wood charcoal, (IV) animal charcoal, (V) gas carbon, and (VI) coke.

I. The purest variety of **coal** is known as *anthracite*, which is an amorphous, black, hard, and somewhat lustrous body, is rather hard to ignite, and has lost all its organic structure. From this there is a regular graduation through *cannel* and *bituminous coals* of all varieties to *lignite*, or *brown coal*, which is sometimes only scarcely altered wood. All coal is derived from primitive vegetation, changed and consolidated by heat and pressure. Anthracite is found where the strata have

TABLE I
CARBON CONTENT OF COALS

Coal	Fixed Carbon Per Cent.	Volatile Matter Per Cent.
Anthracite.....	97.0 to 92.5	3.0 to 7.5
Semianthracite.....	92.5 to 87.5	7.5 to 12.5
Semibituminous.....	87.5 to 75.0	12.5 to 25.0
Eastern bituminous.....	75.0 to 60.0	25.0 to 40.0
Western bituminous....	65.0 to 50.0	35.0 to 50.0
Lignite.....	under 50	over 50

been most exposed to heat or disturbed by volcanic motions; bituminous where the strata are nearly or quite horizontal; while brown coal is much more recent in age, being generally tertiary. The carbon content of the various coals is shown in Table I.

II. **Lampblack** is the soot or amorphous carbon obtained by burning bodies rich in carbon with an insufficient supply of air. Resin, petroleum, tar, or some of the oily products obtained from petroleum are burned with less air than is required for perfect combustion, the smoky products of this combustion passing into chambers hung with coarse cloths, on which the lampblack is deposited. The finest grades of lamp-

black are prepared by depositing the soot on metal cylinders revolving over the burners. Lampblack is purified by heating it in closed vessels.

Diamond black is an extremely pure quality of lampblack made by the imperfect combustion of natural gas, particularly that of the Ohio petroleum regions. Lampblack is used as a pigment for both oil and water colors as well as for liquid and drawing ink. It forms the chief ingredient in India ink and printing ink, and in the preparation of some kinds of leather.

III. **Wood charcoal** is a form of carbon prepared from wood burned with but little access of air. Billets of wood are built up into a heap, Fig. 4, around stakes driven into the

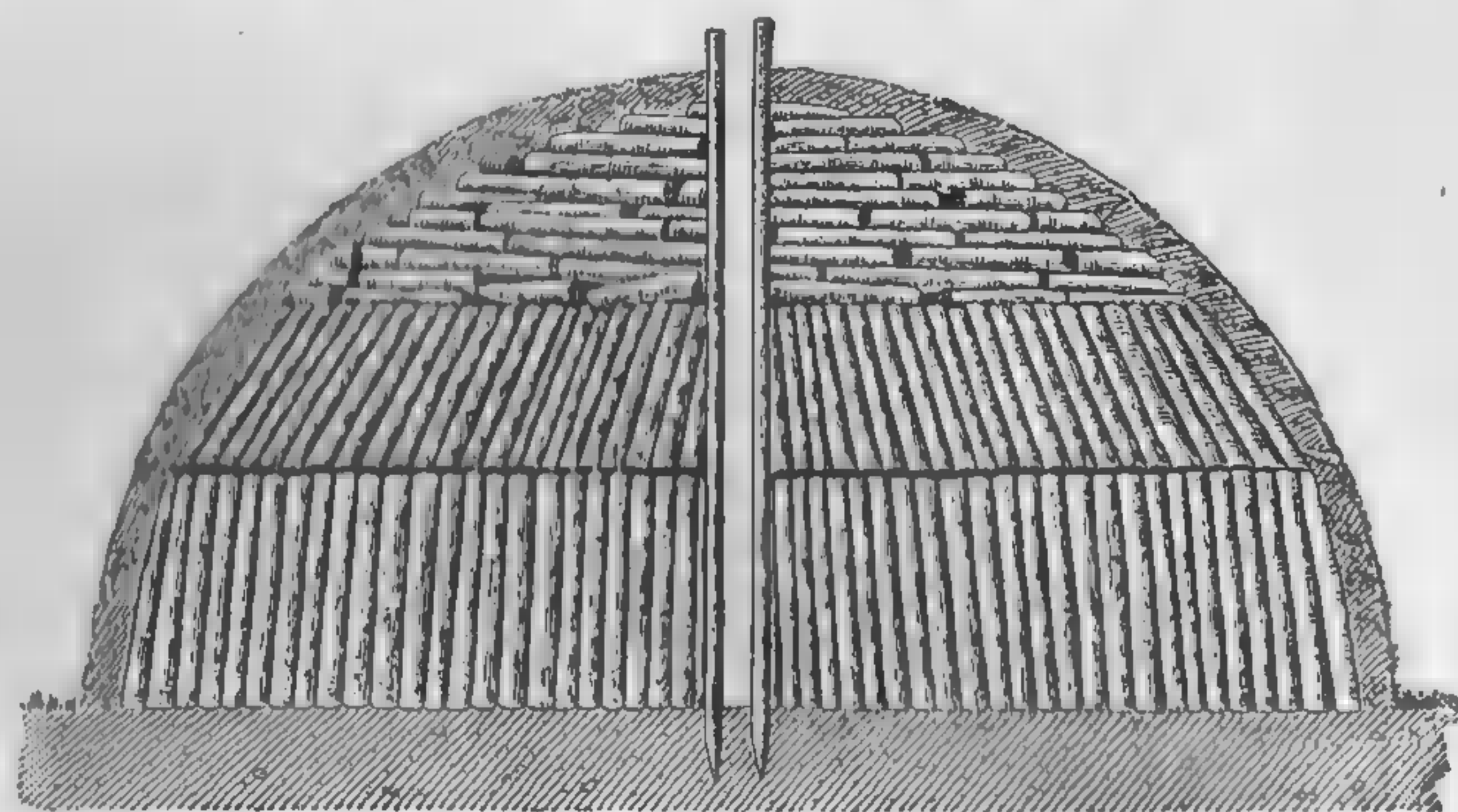


FIG. 4

ground and the heap is then covered with earth or sand. The heap is fired at openings left at the bottom of the pile. For making fine charcoal, such as that of willow, the wood is burned in iron cylinders or retorts. In this method, which is a process of destructive distillation, the volatile products such as wood spirits, pyroligneous acid, and tar are collected.

Good charcoal has a pure black color, and a glittering fracture. It is used as a fuel, a polishing powder, an absorbent of gases and aqueous vapor, as a non-conductor of heat, in fireworks, in gunpowder, and in electricity.

IV. **Animal charcoal**, or *bone black*, is obtained by the calcining of bones in closed vessels. These vessels are either retorts similar to those in which coal is distilled for the

production of illuminating gas, or they are earthenware pots piled up in kilns and fired. After being burned the bones are ground in fluted rolls, and the dust removed.

Animal charcoal is a black, porous mass, used as a decolorizing and filtering agent in sugar refining and in other manufacturing processes.

V. **Gas carbon**, next to lampblack, is the purest form of amorphous carbon. It is formed, as its name implies, in the manufacture of coal gas. It occurs as an iron-gray deposit in the upper part of the retorts. Gas carbon is a good conductor of heat and electricity and is used for batteries and as carbon poles for electric lights.

VI. **Coke** is one of the products of the distillation of coal in ovens and retorts. It bears the same relation to coal that charcoal does to wood. Coke was originally produced by burning coal in heaps, with a limited supply of air. This occasioned a considerable loss of coal and led to the building of coke ovens, the coke produced in this way being found to be much harder, denser, and less combustible than that made in open heaps.

The most efficient method of coking is by means of coke ovens. There are many kinds of coke ovens, but the principle and object are the same in all. The simplest oven is the beehive. Beehive ovens are built of brick and are charged from the top from coal cars running on rails on the top of the ovens. The volatile matter escapes through the charging openings, and the coke is removed through a door in the front of the oven. After the coal has been heated for about 30 hours the coke is raked out and quenched with water. The heat required to carry on the combustion is usually obtained by the burning of the volatile gases of the coal.

The ovens most frequently used at the present time are the by-product ovens. These are more economical than the beehive ovens, as they utilize the gases given off and save the products of distillation of the coal. These ovens are long and narrow and have a door at each end; the roof is supported by heavy masonry. A zigzag flue runs along each side of the oven, and the gases pass alternately from the front to the

back through the flue to a return flue leading to the chimney at the back. The coal is charged through holes in the roof, which are then tightly closed. The distilled gases pass through an opening in the roof connected with a hydraulic main. In the hydraulic main the gases mix with those from the other ovens, and are passed through purifiers to remove the tar and other condensable matter. The purified gas is then forced by fans through pipes passing underneath the ovens to branch pipes, where it is burned, heating the ovens. The blast is preheated by passing through channels in the heated masonry. After about 24 hours the coke is pushed out of the ovens by means of a mechanical ram to a space in front of the ovens, where it is quenched, the ram is withdrawn, and the ovens recharged while still hot.

5. One of the most remarkable and useful properties of carbon, the absorption of gases, depends on its being infusible and non-volatile. The infusibility of charcoal renders it extremely porous, thus providing a very large surface to a given mass for gases to condense on. Animal charcoal possesses a higher absorbing power than wood charcoal. Wood charcoal has the property also of absorbing the unpleasant odors arising from decaying bodies and, when in contact with air, of oxidizing and destroying them. For this reason coarsely powdered charcoal is exposed in shallow trays to the air to be sweetened, as in the wards of hospitals, etc. Water is often filtered through charcoal to remove any organic and soluble coloring matters. This aerates the water as well.

6. The great difference in the properties exhibited by the diamond, graphite, and charcoal naturally leads to the belief that they consist of dissimilar carbon molecules. Very recent researches have shown that the difference in the character and properties of these three varieties of carbon is due to a difference in the internal energy of each, the diamond having the most internal energy, and charcoal having the least.

7. Although carbon shows a remarkable indisposition to unite directly with other elements, the compounds it forms with hydrogen are very numerous. It was at first thought that

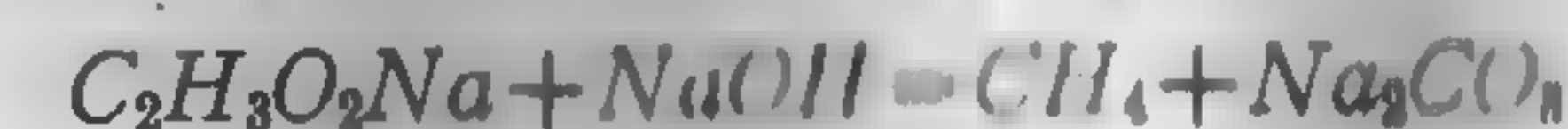
these compounds could be formed only by the growth of organized matter, and they are treated in the Sections on organic chemistry. It is now known that these compounds can be prepared in the laboratory, and that they are subject to the same laws as are the inorganic compounds. As the compounds of carbon and hydrogen are so numerous only three of the simplest compounds will be treated here: *methane*, CH_4 ; *ethylene*, C_2H_4 ; *acetylene*, C_2H_2 .

METHANE

Formula CH_4 . *Density* 8.016. *Specific gravity* .551. *Molecular weight* 16.03.

8. **Occurrence.**—Methane occurs free in nature, being evolved during the decomposition of dead vegetable matter confined under water; hence, it is found in marshy districts, and has thus received its common name of *marsh gas*. On watching stagnant water, bubbles of the gas may be seen to arise; these may be collected by inverting a jar, filled with water, in the pool. During the changes that have occurred while coal has been forming from vegetable growths, methane has also been evolved and has remained imprisoned within cavities of the coal itself. As the coal is removed by the miner, the gas escapes from these cavities into the mine, and, mixing with the air, forms the explosive mixture known as *firedamp* that has caused so many colliery accidents. It often occurs in the vicinity of salt wells, as in Kanawha, W. Va. It is the principal constituent of the so-called natural gas that has come so extensively into use in some cities for purposes of lighting and heating.

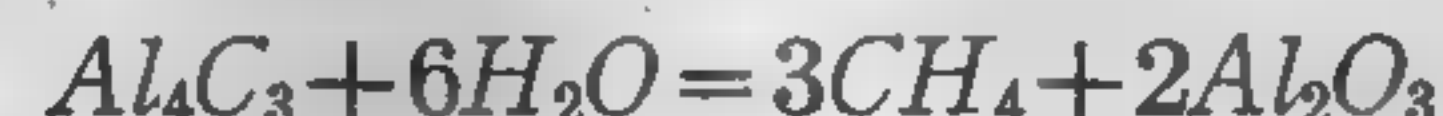
9. **Preparation.**—Methane is best prepared by heating a mixture of sodium acetate and sodium hydrate. The methane is formed according to the following equation:



It is also obtained when carbon monoxide and hydrogen are treated with an electric spark, thus:



Methane is obtained in a pure condition by the action of water on aluminum carbide, thus:



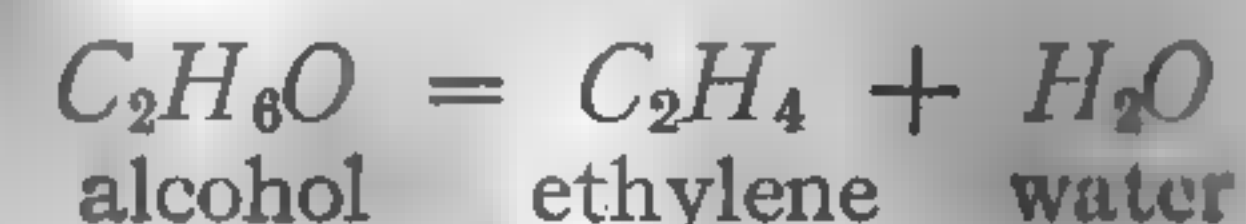
10. Properties.—Methane is a light, colorless gas, and was formerly sometimes called *light carbureted hydrogen*. It is odorless and tasteless, and is but slightly soluble in water, but more readily soluble in alcohol. It is not a supporter of combustion, but burns with a non-luminous flame, resembling that of hydrogen, but slightly tinged with yellow. It forms an explosive mixture with oxygen or air, and is the cause of the serious explosions that sometimes happen in the coal mines. By the action of chlorine on methane, its hydrogen is gradually replaced by chlorine, forming, successively, the compounds CH_3Cl , CH_2Cl_2 , $CHCl_3$, and CCl_4 . It constitutes the first member of a homologous series of hydrocarbons known as the *marsh-gas series*, the successive members increasing uniformly by CH_2 . They are all saturated substances, having the general formula C_nH_{2n+2} ; that is, they contain twice as many atoms of hydrogen as of carbon, plus 2. They constitute the essential portion of the various native petroleum.

ETHYLENE

Formula C_2H_4 . Density 14.016. Specific gravity .970. Molecular weight 28.032.

11. History and Occurrence.—Ethylene, also known as *ethene*, *olefiant gas*, or *heavy carbureted hydrogen*, was discovered in 1796 by four Dutch chemists, Deiman, Paets von Troostwyk, Bondt, and Lauwerenburgh. It is one of the most important constituents of coal gas, being formed when the coal is subjected to destructive distillation; it has been found in small quantities among the gases of coal mines.

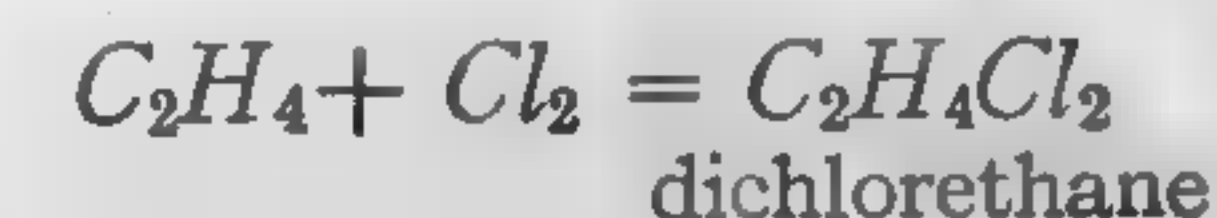
12. Preparation.—Ethylene is most readily prepared by the action of sulphuric acid on alcohol, when the acid abstracts the elements of water from the alcohol:



This equation exhibits only the final result, the chemical change itself being evidently more complicated.

EXPERIMENT.—Mix in a large flask, fitted with a delivery tube, 1 part of alcohol with 5 parts of concentrated sulphuric acid, and heat very gently. Ethylene is readily evolved, and may be collected in jars over water. It will be found advantageous to mix the alcohol and acid with dry sand to a thick paste before heating; the sand is added to prevent frothing toward the end of the evolution of the gas.

13. Properties.—Ethylene is a colorless, irrespirable gas, having usually a sweet ethereal odor. It ignites readily and burns readily with a bright luminous flame that evolves considerable quantities of smoke. It is soluble in about eight times its volume of water, and slightly soluble in alcohol and water. It liquefies at $-1.1^\circ C$. and at a pressure of 43 atmospheres, or at $-103^\circ C$. at ordinary pressure. When mixed with 3 volumes of oxygen, it explodes violently on the approach of a flame. It is decomposed by the electric spark, the carbon being deposited and twice its volume of hydrogen remaining. Ethylene unites directly with an equal volume of chlorine to form an oily liquid of the composition $C_2H_4Cl_2$:

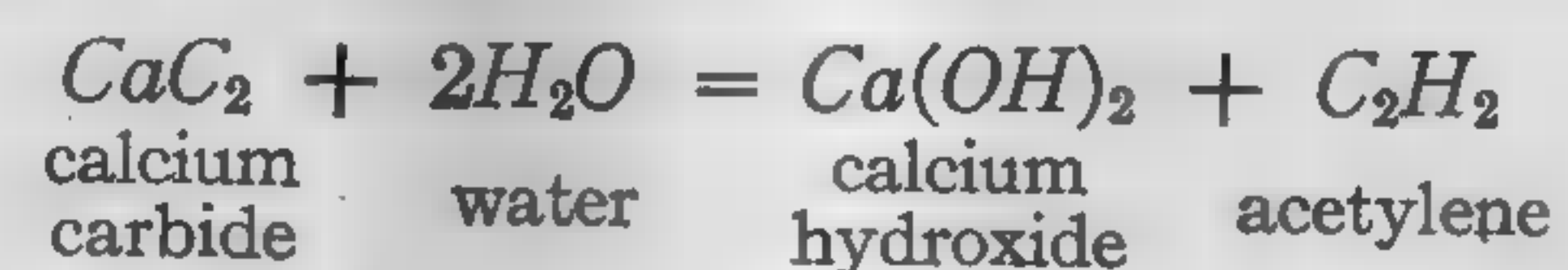


ACETYLENE

Formula C_2H_2 . Density 13.01. Specific gravity .910. Molecular weight 26.016.

14. Acetylene was discovered by E. Davy in 1836, and investigated by Berthelot in 1860. It is produced during the combustion of many hydrocarbons in a limited supply of air; thus, when a Bunsen burner lights at the bottom of the tube, acetylene is produced in considerable quantities. It may be prepared by the direct union of carbon and hydrogen at high temperature. The most convenient method of thus preparing the gas is by passing a current of electricity, from a powerful voltaic battery, through two electrodes of carbon enclosed in a glass flask containing hydrogen. It is

now extensively used as an illuminating gas, being prepared by the action of water on calcium carbide:



Acetylene is a colorless, poisonous gas, with a pleasant ethereal odor when pure but when mixed with impurities has a peculiar and disagreeable odor. It is condensable to a liquid under a pressure of 68 atmospheres at 37° C. It is a non-supporter of combustion, and burns with a bright, luminous, but rather smoky flame. It is quite soluble in water, and is also readily absorbed by ammoniacal cuprous chloride, forming a red precipitate of cuprous acetylide that is explosive. This explosive body is sometimes formed in brass gas pipes by the action on them of the acetylene in coal gas, and may have been the cause of fatal accidents. It unites directly with the halogens; for example, the compounds of chlorine with it are $\text{C}_2\text{H}_2\text{Cl}_2$ and $\text{C}_2\text{H}_2\text{Cl}_4$.

ILLUMINATING GAS

15. History and Preparation.—The production of a combustible gas from coal was first observed by Clayton in 1727, though it was not until 1792 that the application of this gas as a means of illumination was successfully carried out by Murdock. In 1802 he lighted in this way Boulton & Watt's works at Soho, near Birmingham, in England. The streets of London were first lighted with gas in 1812, while Paris did not adopt it until 1815.

Illuminating gas is manufactured by the destructive distillation of bituminous coal, though also various other products, such as petroleum, wood, resin, etc., have been used. The general interior arrangement of a gasworks for the manufacture, purification, and collection of coal gas is shown in Fig. 5. The coal is placed in cylindrical iron retorts *A* set in a furnace *B*. As a rule, five retorts are heated by the same fire, such a set of retorts being technically known as a *bench*. The products of the destructive distillation pass from the retort through a tube *C* into a larger horizontal tube *D*,

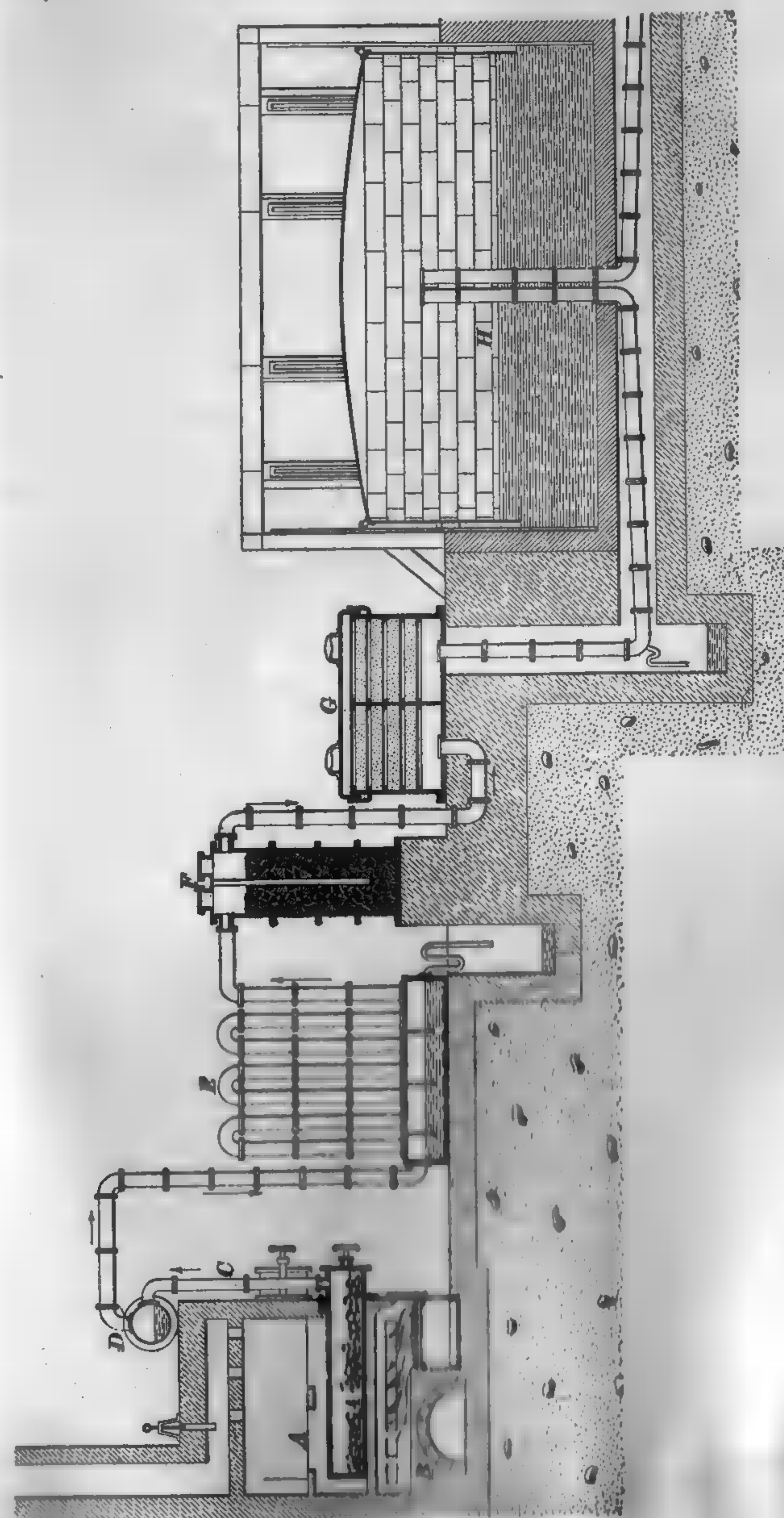


FIG. 5

known as the *hydraulic main*; here the tar and a portion of the water are condensed to liquids. The gas then passes through a series of vertical pipes *E*, and then through the coke box *F*—technically known as the *scrubber*—by which it is still further cooled and the condensable vapors separated. It finally enters the purifier *G*, which consists of a large metallic box, containing, on shelves for this purpose, either dry slaked lime, or, what is preferable, ferric hydrate mixed with lime and sawdust. From this purifier the gas issues, freed from most of its impurities, such as sulphur compounds and carbon dioxide in particular, and is collected in the *gasometer H* for distribution.

The destructive distillation of coal is frequently exhibited on the lecturer's table with the apparatus shown in Fig. 6. The coal is placed into the retort *A*, which is strongly heated; the solid and liquid products (tar, ammoniacal liquor, etc.) distilling over are condensed in the globular receiver *B*. The gas passes on into the first *U* tube, one limb *C* of which contains some red litmus paper for the detection of ammonia, while the other limb *D* contains a piece of paper impregnated with lead acetate, to detect hydrogen sulphide, which will blacken paper thus prepared. The second *U* tube *E* contains enough lime water to fill its bend, which indicates, by becoming milky, the presence of carbon dioxide. At last the coal gas is collected over water in the jar *F*, which is furnished with a jet *G*, from which it may be burned when forced out by depressing the jar in water.

16. Composition and Properties.—Coal gas is a mixture of several gaseous products that vary according to the quality of the coal employed in its manufacture, the temperature at which it is distilled, etc., but consists essentially of hydrogen and methane mixed with variable proportions of ethylene, acetylene, carbon monoxide, carbon dioxide, butylene, nitrogen, oxygen, and hydrogen sulphide. Its specific gravity is about .4, and increases with the illuminating value of the gas.

The illuminating value of a gas is determined by an instrument called a *photometer*, in which the amount of light given by the gas, burning from a jet at the rate of 5 cubic feet per



FIG. 6

hour, is compared with that emitted by a standard candle burning 120 grains of spermaceti in the same time. Coal gas may, under favorable circumstances, rise in its illuminating power as high as 25 to 30 candles, though the average coal gas supplied in our cities rarely amounts to 16 candlepower.

The constituents that contribute most largely to the illuminating value of the gas are acetylene, ethylene, the vapor of benzene, and similar hydrocarbons. The most objectionable constituent is the sulphur, present as hydrogen sulphide and carbon disulphide; this is converted by combustion into sulphurous and sulphuric acids, which seriously injure furniture, pictures, etc. The object of the manufacturer of coal gas is to remove, as far as possible, everything except the essential constituents, and at the same time to obtain as large a volume of gas from a given weight of coal as is consistent with good illuminating value.

The collateral products of the coal-gas manufacture are, in general, two—the ammoniacal liquor and the gas tar. The former consists of the condensed water, holding in solution the ammonia produced from the nitrogenous matters in the coal; the latter is a very complex substance, containing in its lighter portions certain volatile liquids, as benzene and toluene, and certain volatile alkaline bases, such as aniline and chinoline, and, in its heavier portions, certain phenols, as phenol proper (carbolic acid) and cresol; and certain hydrocarbons, as naphthalene and anthracene. All these collateral products, as well as the destructive distillation of coal, are more minutely treated in the Sections on organic chemistry.

CARBON AND OXYGEN

17. There are two well known oxides of carbon, namely, *carbon monoxide*, CO , and *carbon dioxide*, CO_2 . The former is the product of the incomplete oxidation of carbon, the latter the final product of the oxidation of carbon. It is the most important and should therefore be studied first.

CARBON DIOXIDE

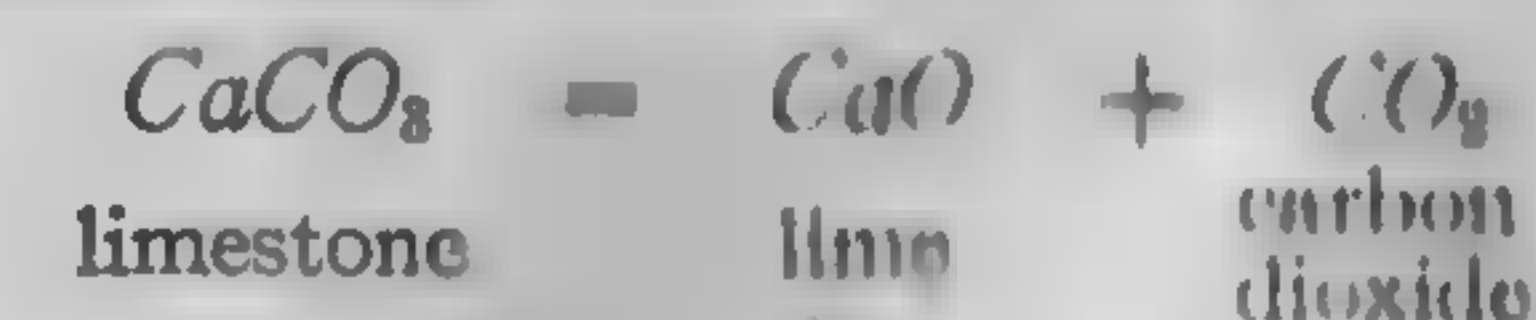
Formula CO_2 . *Density* 22. *Specific gravity* 1.529. *Molecular weight* 44. *1 liter weighs* 1.965 grams.

18. *History*.—It has been stated that carbon dioxide—sometimes erroneously called *carbonic-acid gas*—is a component of the air. It was the first gas distinguished from it, being noticed as a distinct substance by Paracelsus in 1520, while soon after Van Helmont obtained it from limestone—whence he called it *chalky air*—and noticed also its production in the fermentation of sugar, and in the burning of charcoal. Black showed in 1757 that alkalies absorbed it and that its compounds effervesced with acids. Lavoisier in 1775 determined its composition synthetically by burning carbon in oxygen.

19. *Occurrence*.—Carbon dioxide occurs widely distributed in nature. It occurs free in the air, in which it is always present, but of which it forms a small part—about .04 per cent. It is always present, also, in the soil, due to the decomposition of organic matter. It is found in many mineral springs and in the earth in great abundance in the form of carbonates, as limestone, marble, magnesite, dolomite, etc.

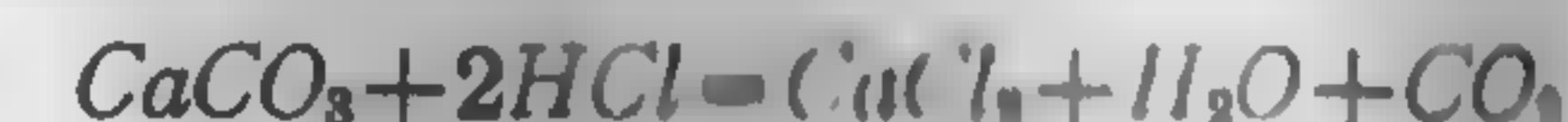
20. *Preparation*.—Carbon dioxide is formed in a number of ways.

1. When limestone is heated it is decomposed into lime and carbon dioxide, thus:



2. By burning wood, coal, or coke in the air.

3. By the action of dilute hydrochloric acid on marble or chalk, forming calcium chloride and carbon dioxide, according to the equation:



In this method the gas is purified by being passed through a solution of sodium bicarbonate and then dried by passing through a tube containing calcium chloride.

21. Properties.—Carbon dioxide is a colorless gas with a slightly pungent odor and acid taste—best described as being those of a freshly opened bottle of soda water. It is heavier than air, its specific gravity being 1.529. At 15° C. and at ordinary pressure, carbon dioxide is soluble in about its own volume of water; as the pressure increases—the temperature remaining constant—another volume of the gas is absorbed for each atmosphere of pressure added. As the gas, however, is condensed in the same ratio, according to Mariotte's law—the volume of any gas is inversely and its density is directly as the pressure to which it is subjected—it follows that the volume of the gas dissolved by water is actually the same at all pressures, while the weight is directly proportional to the pressure.

Carbon dioxide is non-combustible and will not support combustion or respiration. The flame of a candle is at once extinguished when inserted into the gas. Although carbon dioxide is poisonous when inhaled, it does not have any toxic properties but kills by exclusion of oxygen from the lungs. According to some authorities air containing as high as 5 per cent. of carbon dioxide can be breathed without serious effects, but experiments have shown that .2 per cent. of carbon dioxide in the air tends to lower the action of the pulse.

Being heavier than air, carbon dioxide may be collected by displacement of air and may be poured from one vessel to another. The danger in entering old wells, cellars, and other confined places, is due to the accumulation of carbon dioxide at the bottom of the well or along the floors of old cellars, about 12.5 per cent. of the gas causing suffocation. About 5 per cent. of the gas in air will extinguish a lighted taper, but will support respiration for a time.

22. At ordinary temperatures and under a pressure of about 55 atmospheres, carbon dioxide condenses to a clear, mobile liquid having a specific gravity of .85, and boiling at -80° C. When liquid carbon dioxide is allowed to evaporate rapidly it forms a white crystalline mass and lowers the temperature of the surrounding air.

Liquid carbon dioxide is insoluble in water but is soluble in alcohol and ether. It dissolves iodine but has no action on sulphur, phosphorus, sodium, or potassium. The liquid may be prepared on a small scale by treating ammonium carbonate with sulphuric acid in a strong sealed bent tube when the gas will be liquefied by its own pressure. It may also be obtained on a larger scale by using the apparatus invented by Thilorier, in which the gas is liquefied by its own pressure, or that of Natterer, in which the pressure is produced mechanically.

Fig. 7 represents Bianchi's modification of Natterer's condensing pump. The piston is solid, and is worked by a crank and flywheel. The receiver at the top of the pump barrel is made of heavy bronze, and has a tight valve below, and a screw plug above, by which the liquefied carbon dioxide may be drawn off. The tube leading to the pump serves to convey the carbon dioxide. As the pump is worked, the pressure in the receiver increases until it reaches about 38.5 atmospheres—the receiver being packed in ice—when each additional stroke of the pump liquefies the gas which is forced into it. In this way, $\frac{1}{2}$ kilogram of liquid carbon dioxide may be obtained in a very short time.

The receiver is then removed from the pump and inverted, and the gas allowed to escape into a peculiarly constructed cylindrical box of metal, which, in the course of a few seconds, is filled with the solid carbon-dioxide snow. At present liquid carbon dioxide is brought into the market in steel cylinders and is used in various ways.

23. If liquid carbon dioxide is forced into or blown through a coarse canvas bag, a portion of it passes through the bag as a



FIG. 7

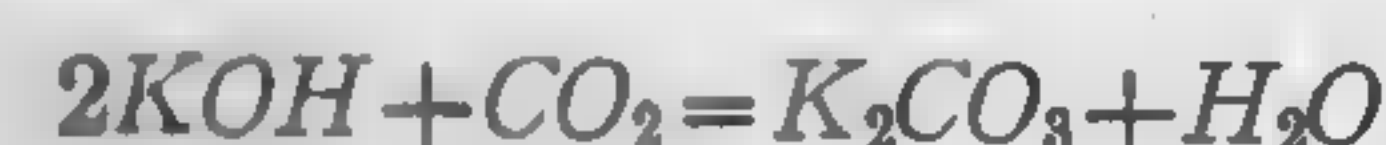
gas while the solid snow-like crystalline mass caused by the rapid evaporation of the liquid remains in the bag. This can be compressed into the solid carbon dioxide. Solid carbon dioxide evaporates very slowly, and melts at about -60°C .

24. Carbon dioxide dissolves in water, forming a dibasic acid. This acid forms two classes of salts, the carbonates, which correspond to the formula $M'_2\text{CO}_3$, and the bicarbonates, corresponding to the formula $M'\text{HCO}_3$. The former, a neutral salt, has a basic reaction, owing to the slight acidity of carbonic acid. Most all acids decompose the carbonates into carbon dioxide and the oxide of the metal.



FIG. 8

If carbon dioxide is passed into a solution of potassium hydrate, the carbon dioxide is absorbed, forming potassium carbonate and water, thus:



The water, in turn, dissolves the carbonate formed. This reaction is used as a means of determining the amount of carbon dioxide in a mixture of gases. The proportion of carbon dioxide is determined either from the increase in weight of the potassium hydrate after it has absorbed the carbon dioxide or from the diminution in volume of the gas after having been treated with potassium hydrate. In the latter case the gas is carefully measured over mercury, in an instrument similar to that shown in Fig. 8, the temperature and atmospheric pressure being taken into consideration. A little concentrated solution of potassium hydrate is introduced into the opening of the measuring tube beneath the surface of the mercury, by means of a curved pipette or syringe. The tube is shaken for a few seconds, to assist in the absorption of the gas, and, after a rest of a few minutes, the diminution of volume is read off. In some cases a ball of moist solid potassium hydrate attached to a bent wire is used in place of the potassium-hydrate solution.

CARBONIC ACID

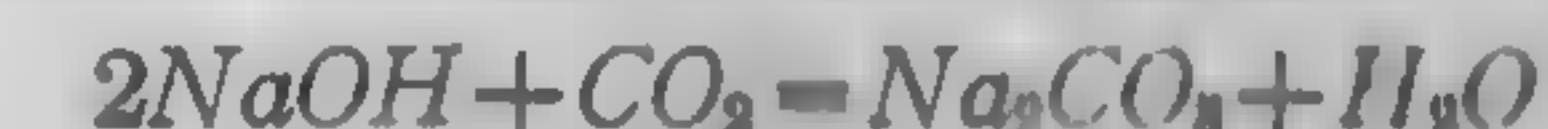
Formula H_2CO_3 . Molecular weight 62.016.

25. Carbonic acid is produced by the solution of carbon dioxide in water, according to the equation:



It is, however, unstable, and has not been obtained free from water, on account of decomposing too readily into water and carbon dioxide on slightly raising the temperature or by freezing it. The solution in water is distinctly, though feebly, acid. It possesses the pungent odor and agreeable acid taste so well known in so-called soda water, which, in fact, is simply made by dissolving carbon dioxide in water under a certain pressure. The existence of this acid is proved by the fact that the aqueous solution will redden blue litmus paper, although the dry carbon dioxide has no action on litmus paper.

26. Salts of Carbonic Acid.—Although carbonic acid itself is very unstable, its salts, the carbonates, are very stable compounds. Being a dibasic acid, normal and acid salts are formed. When carbon dioxide is passed into solutions of the alkali hydrates the normal carbonates, which are soluble in water, are formed according to the equation:



If these carbonates are again treated with carbon dioxide, the acid salt, or bicarbonate, is formed thus:



The normal carbonates of the alkaline earths can be prepared also in the same way, but these are insoluble in water. The alkaline-earth carbonates dissolve in an excess of carbonic acid, forming the bicarbonates.

Carbonates may be either normal, acid, or basic. A *normal carbonate* is one in which all the hydrogen of carbonic acid has been replaced by a metal or group of metals, as sodium carbonate, Na_2CO_3 , or barium carbonate, BaCO_3 . An *acid carbonate* is one in which only one-half of the hydrogen has been

replaced by a metal, as acid sodium carbonate, or sodium bicarbonate, NaHCO_3 . A *basic carbonate* is a normal carbonate in combination with an oxide or hydroxide of the metal, as in white lead, basic lead carbonate, $2\text{PbCO}_3\text{Pb(OH)}_2$.

Strange as it may appear, all the normal carbonates of the alkalis have an alkaline reaction, and the bicarbonates or acid carbonates of the alkalis are neutral to phenolphthalein.

27. Hard and Soft Waters.—The student will have noticed, from daily experience, that certain kinds of water, when mixed with a very small quantity of soap, immediately produce a lather, and that the water acquires that peculiar feel to the hands which is generally known as *soapiness*; such water is termed **soft water**. Other waters, when used with soap for washing purposes, do not lather at all readily, and do not cause soapiness until a considerable quantity of soap has been consumed. When lather is actually formed, there will be found, on examination, a layer of scum on the surface of the water; such water is termed **hard water**.

Without going into the details of the composition of soap and its reaction with water when used for washing, it may be explained that soluble salts of calcium and magnesium decompose soap, forming a precipitate that constitutes the scum found when washing with hard water. Consequently, if water containing calcium salts in solution is employed for washing purposes, sufficient soap must first be added to precipitate these salts before any is available for cleansing; hence, hard waters are neither so agreeable nor so economical for washing purposes.

The principal calcium and magnesium salts found in water are the carbonate and the sulphate. The carbonates may be precipitated by the act of boiling and any hardness due to their presence may be thus remedied. Consequently, any hardness produced by carbonates of calcium or magnesium is termed *temporary hardness*.

The sulphates and chlorides of calcium and magnesium are not precipitated by boiling, as their solution is caused by the water itself, and not by water plus carbon-dioxide gas.

Therefore, hardness due to the presence of sulphates or chlorides of calcium or magnesium is called *permanent hardness*.

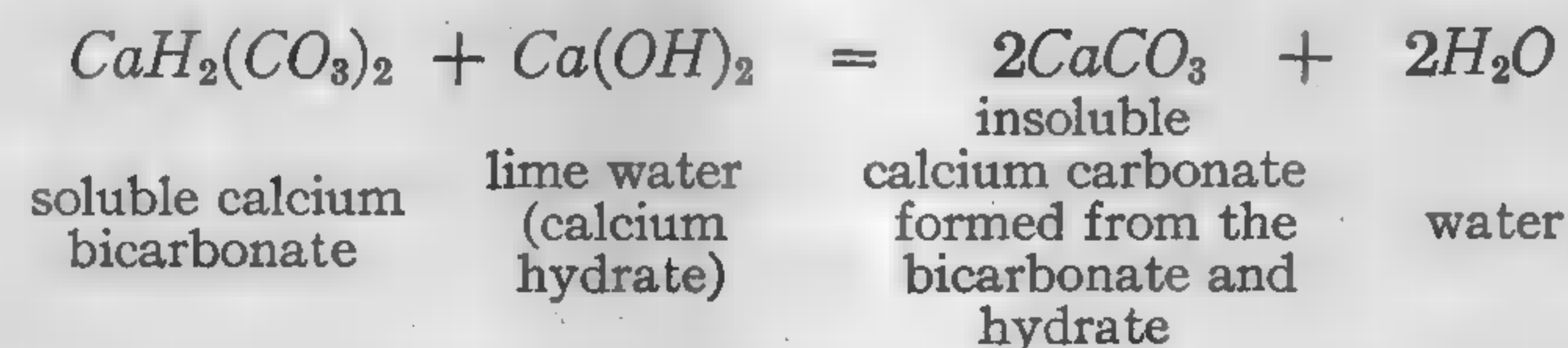
The hardness of most waters is partly temporary and partly permanent, the two together constituting what is known as the *total hardness* of the water.

The hardness of the water is usually tested by taking a measured quantity of the water and adding thereto in a stoppered bottle a solution of soap in alcohol of a known strength. This is introduced in small quantities at a time from a measuring instrument, such as a burette, the water being well shaken after each addition. As soon as a lather that stands unbroken for about 5 minutes is thus produced, the quantity of soap solution used is read off; from which the total hardness is determined. A sample of the water is next boiled until the carbonates are precipitated; then, after certain precautions the hardness is again determined with the soap solution. This gives the temporary hardness, which is the difference between the total and the permanent hardness.

28. Processes of Softening Water.—Water may be softened, to the extent of the removal of the temporary hardness, by the act of boiling for some minutes. Potassium, and sodium carbonates precipitate calcium and magnesium salts, and themselves possess detergent, or washing, properties; therefore, these salts will remove all hardness, whether temporary or permanent. One of the characteristics of potassium and sodium carbonates is the power they possess of imparting a soapy feeling to pure water. Ordinary washing soda, or soda crystal, is commercial sodium carbonate.

A most interesting process for the softening of water is the one named *Clark's process*. It depends on the facts that calcium bicarbonate is soluble in water while the normal carbonate is insoluble; and that the hydrogen of the soluble bicarbonate may be replaced by calcium, forming the insoluble normal carbonate. To soften water by Clark's process, lime water is added in sufficient quantity to exactly replace the hydrogen of the bicarbonate. The whole of the calcium, both that originally present in the water as carbonate and

that added as hydrate, is precipitated, and the temporary hardness is thus removed. The chemical reaction is represented in the following equation:

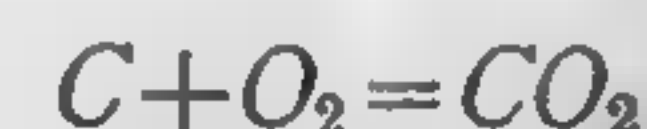


The precipitated calcium carbonate is removed either by allowing it to subside or by filtration.

CARBON MONOXIDE

Formula CO. Density 14. Specific gravity .967. Molecular weight 28.

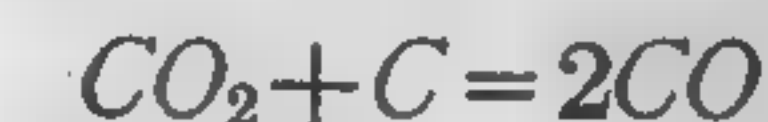
29. History and Occurrence.—Carbon monoxide was discovered by Lussone in 1776, and independently by Priestley in 1783; its true nature and exact composition was determined by Woodhouse in 1800. Every one is familiar with the appearance of a coke or charcoal fire, or of a coal fire that has burned perfectly clear and smokeless—the whole mass glows with a bright red heat, and hovering over the top are lambent blue flames. The origin of these may be traced in this way: In the lower parts of the grate, where air enters the fire, carbon dioxide is formed according to the equation:



This carbon dioxide makes its way upwards through the red-hot carbon, and becomes changed by reduction to carbon monoxide, and an inflammable gas is thus produced. The same effect is produced in the following manner:

EXPERIMENT.—Loosely fill an iron tube with fragments of charcoal; fit to each end stoppers with pieces of small glass tube passed through; place it in a combustion furnace and raise to a red heat. Then pass a slow current of carbon dioxide through the tube and light the gas as it emerges; it burns with the same blue flame as is seen playing over a coke or charcoal fire.

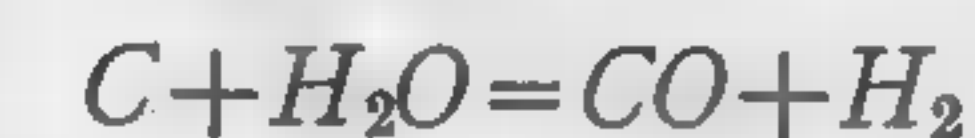
Evidently, then, the gas is changed; for carbon dioxide is non-inflammable. The change is thus represented:



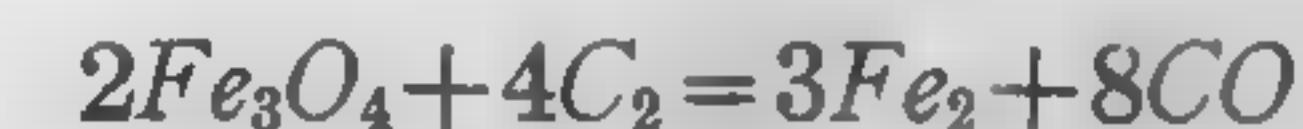
When carbon is burned without a sufficient supply of air, carbon monoxide is formed as one of the products of combustion.

30. Preparation.—Additional to the reaction described in the experiment in Art. 29, carbon monoxide may be prepared by heating within an iron cylinder a mixture of calcium carbonate (chalk) and charcoal. The calcium carbonate is decomposed into calcium oxide and carbon dioxide, which later is converted by the charcoal into monoxide.

A mixture of carbon monoxide and free hydrogen is produced in abundance by passing steam over or through charcoal heated to bright redness; the reaction occurring may be expressed by the following equation:

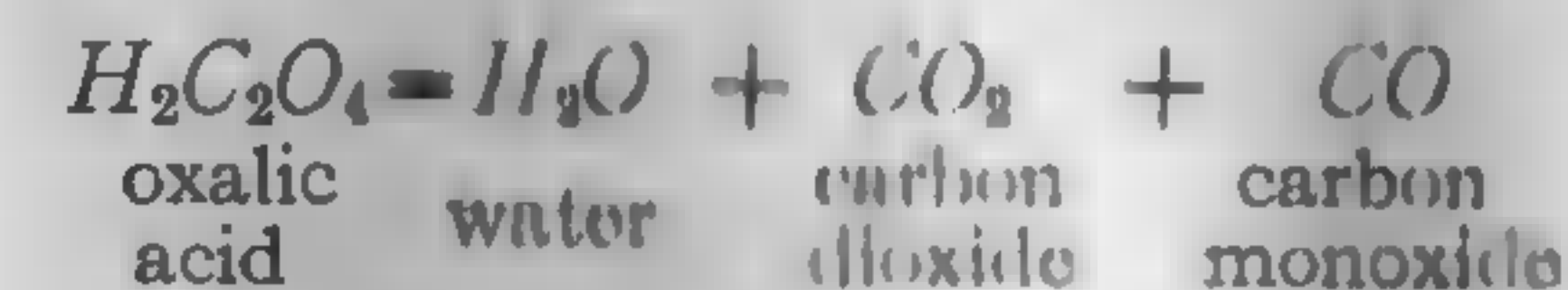


It may further be prepared by the incomplete combustion of carbon, as when charcoal and blacksmith's scales are heated together, according to the equation:



For laboratory purposes the gas is most conveniently prepared by heating certain organic compounds with concentrated sulphuric acid; as this body has a very great attraction for water, it decomposes many substances containing hydrogen and oxygen, and assimilates the water, the remaining atoms rearranging themselves into whatever other compounds are possible.

Oxalic acid, when treated in this manner, is split up into water, carbon dioxide, and carbon monoxide, thus:



EXPERIMENT.—For the preparation of carbon monoxide from oxalic acid, such an apparatus as is shown in Fig. 9 is needed. The oxalic acid (crystallized) is placed in the flask A and enough sulphuric acid is added to just cover it. The whole is heated in an iron cup filled with sand

(sand bath) *B*. The gases evolved pass into a washing bottle *C*, which is about half filled with a strong solution of potassium hydroxide; in bubbling through this solution the carbon dioxide is absorbed, and the carbon monoxide, thus purified, may be collected over water in the pneumatic trough. As this gas is very poisonous, great care should be taken in its preparation.

31. Formic acid, $HCHO_2$, on being similarly heated with concentrated sulphuric acid, yields pure carbon monoxide, according to the following equation:

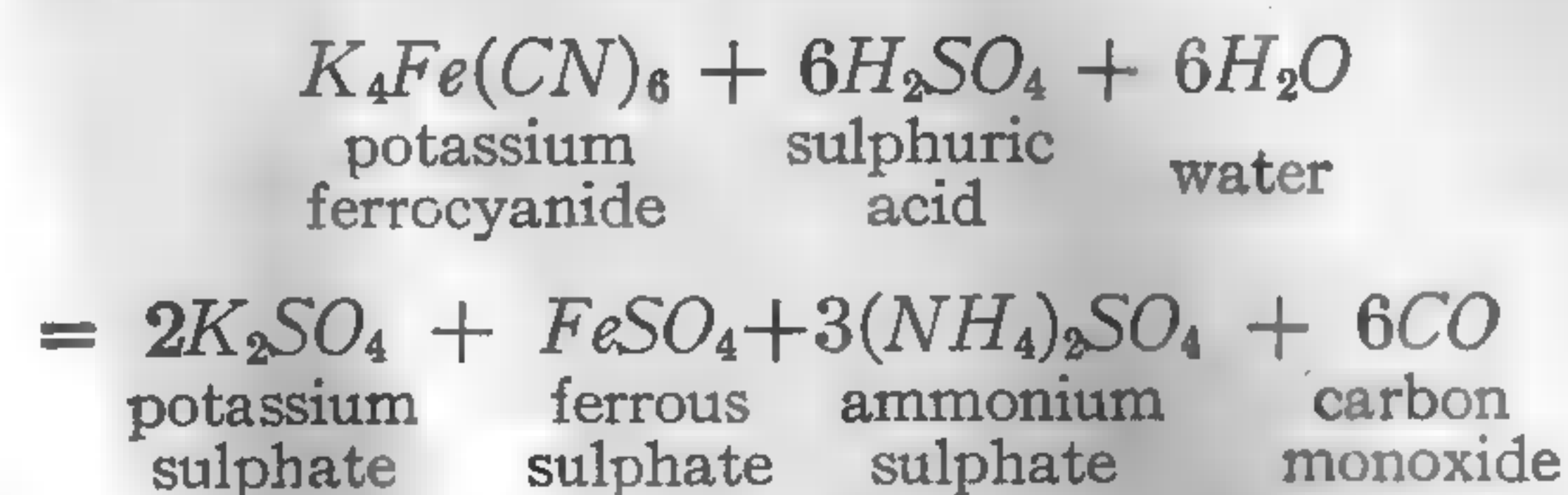


Another method is to heat potassium ferrocyanide, $K_4Fe(CN)_6$,



FIG. 9

with sulphuric acid; the change occurring is rather complicated, but may be expressed by the equation:



When carbon monoxide is required in a state of absolute purity, the former of these two methods is preferable. The latter, though yielding this gas in larger quantities, is, as a rule, accompanied by traces of carbon dioxide as a contamination.

EXPERIMENT 1.—Fit up a 32-ounce flask with a thistle funnel and leading tube, as shown in Fig. 10. The end of this thistle funnel must be pushed down as far as possible without touching the bottom of the flask. Insert, in lumps, $\frac{1}{4}$ ounce (7.09 grams) of commercial ferrocyanide (the quantity in cubic centimeters cannot be very well given, in this case, owing to the irregular size of these lumps, so, in order to be as accurate as possible, only the weights are mentioned) and about 2 ounces (30.8 cubic centimeters) of sulphuric acid. Fix the flask in the retort stand with the end of the leading tube in the pneumatic trough; apply heat carefully. As soon as the gas begins to be evolved, remove the flame, as the action continues with extreme rapidity. When the air is entirely expelled, collect the gas over water, the given quantities being sufficient to fill three pint jars. Sometimes, through lack of sufficient precautions, the gas is produced so violently that the pressure forces the boiling acid up through the funnel. Should this occur, remove the burner at once, take the delivery tube out of the water, and keep well out of the reach of the splashes of falling acid.

EXPERIMENT 2.—Place a light to one jar filled with the gas; notice that the gas burns with a blue flame.

32. Properties.—Carbon monoxide is a colorless, tasteless gas, possesses a peculiar oppressive odor, and is extremely poisonous, producing a painful headache even when present in small quantities in the air. It liquefies only under very great cold and pressure ($-139.5^\circ C.$ and 35.5 atmospheres). It is only slightly soluble in water, 100 volumes of which dissolve 2.434 volumes of the gas at $15^\circ C.$ It is readily combustible, burning in the air or in oxygen with a characteristic lambent blue flame. Though inflammable, it is not a supporter of combustion. When burned, its own volume of carbon dioxide is produced, half of its own volume of oxygen being required:



Mixed with moist air or moist oxygen it forms an explosive mixture. When perfectly dry, however, no explosion occurs and the combination takes place slowly.

It is totally irrespirable, being an active narcotic poison, 1 per cent. of it in the air proving fatal. Radium emanations decompose it into carbon dioxide, carbon, and oxygen.

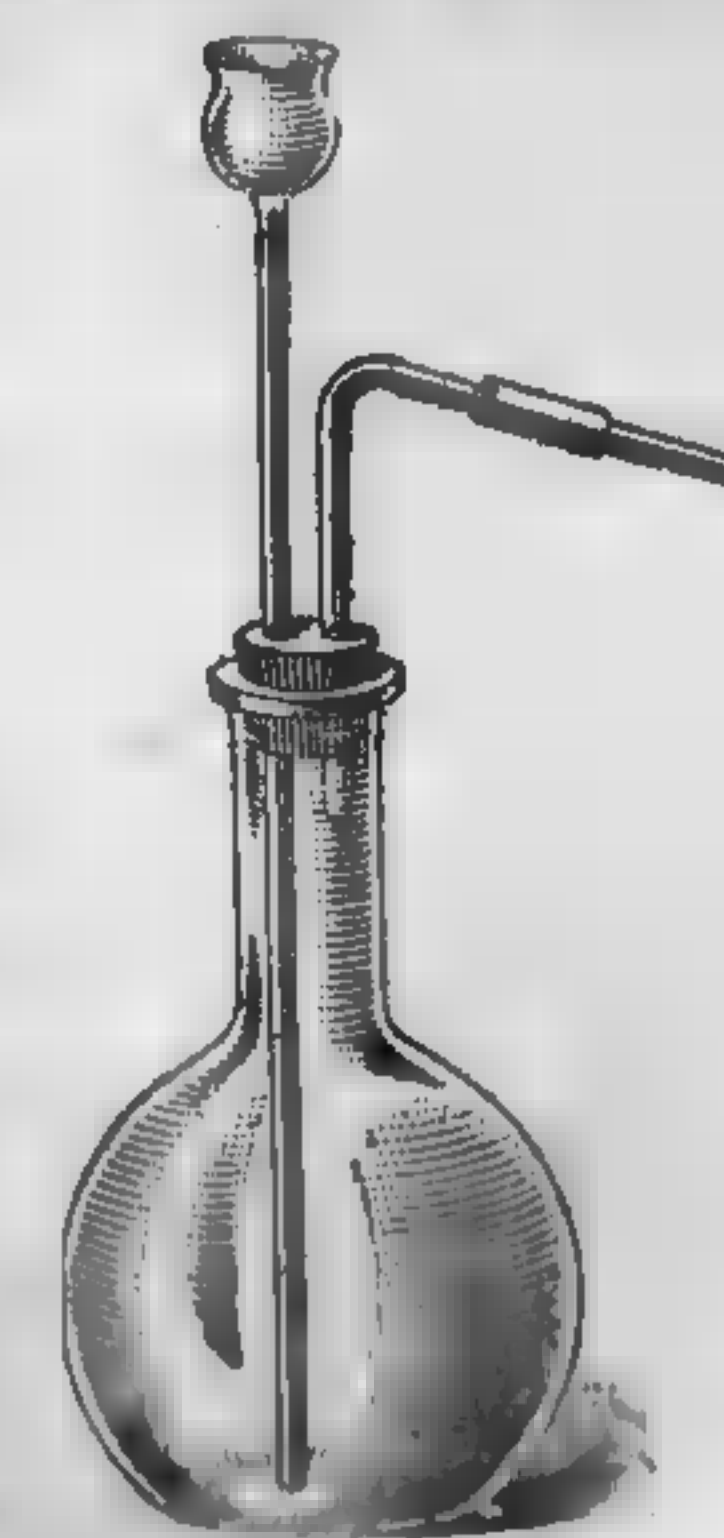


FIG. 10

Carbon monoxide is devoid of acid properties, and, consequently, is without action on lime water.

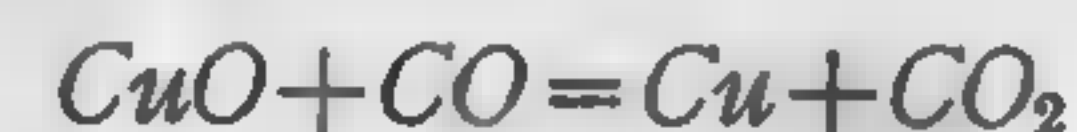
EXPERIMENT.—Add some lime water to a jar of the gas and shake up; no turbidity is produced. Ignite the gas, replace the glass plate, and then shake again; the lime water becomes milky through the presence of carbon dioxide produced by combustion.

33. Carbon monoxide acts as a powerful reducing agent, and is frequently used in metallurgical operations for the production of metals from their oxides.

EXPERIMENT.—Arrange a piece of combustion tubing, about 18 inches in length, in the combustion furnace, and connect—by means of a stopper, a piece of quill tubing, and a rubber tube—with an apparatus evolving carbon monoxide. (The most convenient method of obtaining the gas for this purpose is from oxalic acid and sulphuric acid. The gas may be passed through a wash bottle containing a solution of potassium hydroxide, but the carbon dioxide takes no part in the reaction.) Partly fill the combustion tube with granulated copper oxide, expel the air by passing through it a slow current of carbon monoxide, and then light the furnace. On the tubes becoming red hot, notice that the oxide of copper is reduced to the metallic state.

If wished, carbon monoxide free from the dioxide may be prepared and used for this experiment, and the gas, after its passage through the red-hot copper oxide, may be passed into lime water. The precipitate of calcium carbonate shows the production of carbon dioxide from the reaction of the monoxide and copper oxide on each other.

The following equation shows the chemical change that occurs during this experiment:



This experiment is one that the student cannot perform by himself; but, being a typical experiment performed on the lecturer's table, and one so clearly showing the reducing power of carbon monoxide, it appears highly desirable that the student should become acquainted with it.

Gold and palladium are precipitated from their chloride solutions, and platinic chloride is reduced to platinous chloride by means of carbon monoxide. Carbon monoxide unites with nickel and iron, forming nickel carbonyl, $\text{Ni}(\text{CO})_4$, and ferric pentacarbonyl, $\text{Fe}(\text{CO})_5$, both of which are liquids.

34. The so-called *water gas* is a mixture of carbon monoxide, carbon dioxide, and hydrogen, to which has been added hydrocarbons to increase its luminosity. It is prepared by passing steam over red-hot coke. Owing to the poisonous character of carbon monoxide, the amount permissible in a gas used for illuminating purposes is now fixed by law in most states. The average composition of water gas is generally:

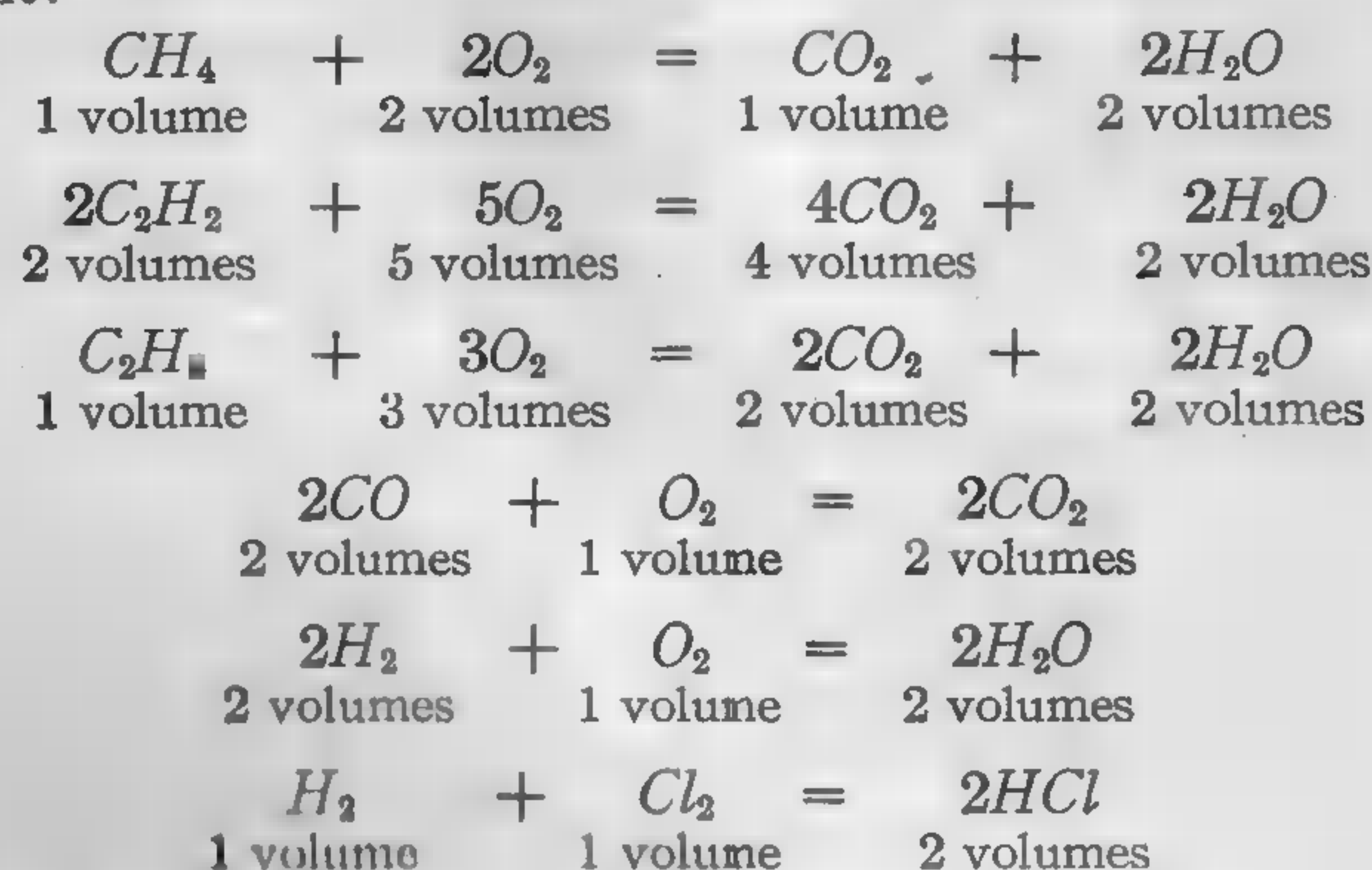
Hydrogen	50 per cent.
Carbon monoxide	40 per cent.
Carbon dioxide	5 per cent.
Nitrogen (from the air and coke)	5 per cent.
	<hr/> 100 per cent.

35. Summary.—There exist two oxides of carbon—carbon monoxide and carbon dioxide. Carbon dioxide occurs in the atmosphere and in combination with lime in limestone; it is most conveniently prepared by the action of an acid, as of hydrochloric, on limestone. It is a colorless gas, with a very faint odor and taste; it may be condensed by pressure; it is soluble in water, is half as heavy again as air, and remains through its weight for a long time in the bottom of brewers' vats, old wells, etc.; it is non-inflammable and a non-supporter of combustion of most substances, but allows certain metals, as potassium and magnesium, to burn in it. The solution of the gas is slightly acid to litmus; it forms a series of important salts.

Carbon monoxide is formed in the burning of coke by the deoxidation of carbon dioxide; the same change occurs if carbon dioxide is passed over red-hot charcoal in an iron tube. It is more generally prepared by the action of sulphuric acid on some organic compounds, as oxalic or formic acids, or potassium ferrocyanide. Carbon monoxide is a colorless, tasteless gas, with a faint, oppressive odor; it is very poisonous; it is slightly soluble in water. It is inflammable and is a non-supporter of combustion; it is devoid of acid properties. It is a powerful reducing agent.

36. Combustion of Methane, Acetylene, and Ethylene.—The combustion of these three bodies affords some

very interesting and instructive examples of the laws of combination by volume. Subjoined are the molecular equations representing the reactions that occur, together with those of some other examples of combustion familiar to the student:



These equations show to a nicety the relation that exists between the volumes of gases and the respective volumes of oxygen required for their combustion. They afford additional illustrations of the method of deducing these quantities from the molecular equations.

As gaseous molecules are assumed (at the same temperature and pressure) to occupy the same space, it follows that the number of molecules of any gas participating in a chemical change represents the number of volumes of the gas concerned.

37. Combustibles.—Combustion is an act of burning, or, to be more explicit, a chemical combination that is so intense as to raise the products to a temperature at which they emit light. It is commonly restricted, however, to the direct union of a substance with oxygen.

It is evident that at least two substances must be concerned in every combustion—the *combustible*, that is, the body that burns; and the *supporter of combustion*, that is, the gas in which the combustion takes place. Those substances that serve as combustibles are naturally very numerous. The

illuminating gases—coal and water—have been mentioned. Of liquids, the vegetable oils known as rape, olive, and turpentine; the animal oils called sperm and lard; and the mineral oils derived from petroleum may be quoted. Of solids from the vegetable kingdom, wood and bayberry wax; from the animal, tallow and its product, stearin; and from the mineral, paraffin and the various sorts of coal, are examples. All these substances, though so different in character and origin, agree in the fact that they contain carbon and hydrogen. Some contain oxygen in addition.

TABLE II
HEAT DEVELOPED DURING COMBUSTION

Substance	In Oxygen Heat Units	In Chlorine Heat Units
Hydrogen	34,462	24,087
Carbon	8,080	
Sulphur	2,220	
Phosphorus	5,747	3,422
Carbon monoxide	2,634	
Methane	13,063	
Ethylene	11,942	
Alcohol	6,909	

38. Heat of Combustion.—Not only do substances in burning give out heat, but the amount of heat evolved by the combustion (or combination with oxygen) of a given weight of any substance is always the same. Thus, whether the substance be burned slowly or rapidly, provided it is burned to the same products of combustion, the total amount of heat generated never varies. Table II gives the number of heat units evolved by the combustion in oxygen and chlorine, respectively, of 1 gram of each substance. A heat unit is the quantity of heat necessary to raise 1 gram of water from 0° to 1°.

Of the elements, hydrogen develops by far the greatest amount of heat on combustion; the next greatest amount is developed by carbon. Of the various compounds of carbon,

carbon monoxide; during its further combustion to carbon dioxide, evolves also a considerable quantity of heat.

39. It will be of interest to compare the amount of heat evolved in the two stages of oxidation of carbon. As carbon monoxide contains, according to its formula, about $\frac{1}{2}$ of its weight of carbon; it is evident that 1 gram of carbon would yield $\frac{2}{1}$ grams of carbon monoxide, and, consequently, that 1 gram of carbon as monoxide would, in its further oxidation to carbon dioxide, evolve

$$\frac{2,634 \times 28}{12} = 6,146 \text{ heat units}$$

But the total number of heat units evolved by the complete combustion of carbon is 8,080. Therefore, 1 gram of carbon evolves in oxidation to the monoxide $8,080 - 6,146 = 1,934$ heat units, and, during further oxidation to the dioxide, 6,146 heat units. The student knows that when the carbon dioxide formed in a fire of carbon passes upwards through red-hot carbon, it is reduced to the monoxide, which in its turn burns on the upper surface of the fire, where there is free access to air. Whenever carbon is burned with a limited supply of oxygen, as where a draft of air is drawn through a furnace containing large quantities of coke or other forms of carbon, the monoxide is the chief product of combustion. This cannot burn until it reaches the air; accordingly in the older forms of furnaces used in metallurgical operations, particularly the blast furnace used for the smelting of iron ores, enormous quantities of carbon monoxide were formed and allowed to burn to waste on the tops of the furnaces. The value of this gas as a fuel is now recognized, and it is consequently drawn from the upper part of the furnaces and utilized for heating purposes.

40. Temperature of Combustion.—Although the absolute amount of heat evolved by the combustion of a unit weight of hydrogen, for instance, is always the same, the temperature produced may vary within certain limits. Thus, first of all, if within a given space, hydrogen is caused to burn in one instance at twice the rate of another, it follows that, as a

greater number of units of heat are evolved in the same period of time, the temperature of that space will be raised proportionately higher. Other causes, also, influence the temperature produced by combustion; for example, a jet of hydrogen, burning the same number of cubic feet per hour, produces a much higher temperature when it burns in oxygen than it does when burning in air.

If 2 grams of hydrogen is burned in oxygen, the heat evolved must raise the temperature of the 17.88 grams of water produced. But, if the oxygen is obtained from air, then not only must there be heated the 15.88 grams of oxygen in the water produced, but also the 53.5 grams of nitrogen with which the oxygen was mixed. The same number of units of heat is in the one case spread over 17.88 grams; in the other, over $17.88 + 53.5 = 71.38$ grams of gaseous matter—from which it follows that the temperature in the first instance must be very much higher than in the second.

41. Structure of Flame.—Flame is defined as a gas combining with oxygen becoming heated to a temperature at which it becomes visible, that is, until it emits light. Some substances, like sulphur and phosphorus, give a flame when burned in air or in other gas, such substances being converted into gases or vapors at the temperature of combustion. The presence of a combustible gas or vapor is one of the necessary conditions for the existence of the flame. Pure carbon becomes incandescent because it is non-volatile. A diamond or a piece of charcoal will burn in oxygen with a steady glow, but without flame, because it is not capable of conversion into vapor.

To obtain a brilliant light from a flame it is essential that it should contain particles that are capable of incandescence when highly heated. The flame of an oxyhydrogen blowpipe is very pale, but when the flame is made to heat a column of lime, an intense light is obtained, due to the lime being heated to incandescence.

Phosphorus, when burning, emits a very luminous flame, owing to the oxide formed in the combustion being heated to incandescence.

From these statements it can be seen that the incandescent matter does not necessarily have to be a product of the combustion, as any solid in a finely divided state will confer illuminating power to a flame. If finely divided carbon is blown from a bottle, fitted as shown in Fig. 11, into a hydrogen flame, the flame will be rendered highly luminous. The luminosity of all flames is due to the presence of highly heated carbon in a very minute state of division. Hydrogen and methane give pale flames, because they burn directly to carbon dioxide and water; on the other hand, ethylene and other hydrocarbons burn with a bright flame, because, at the temperature of combustion, they decompose into methane and carbon, and the particles of the latter become incandescent in the intense heat.



FIG. 11

42. When a candle is lighted a portion of the wick burns until the heat reaches the wax of which the candle is made. This wax then melts and is drawn up the wick and decomposed into various hydrocarbons, which ignite, combine with the oxygen of the air, and produce the flame. The flame in turn melts more of the wax around the wick and the process just described is repeated.

The structure of a candle flame is common to all flames obtained by the combustion of a gas. The flame of a candle consists of four cones, as shown in Fig. 12. The inner cone, which appears black, contains the unaltered gases. These cannot burn because of the absence of air. The presence of unburned gases in this center cone can be shown by holding one end of a glass tube in this cone, when the gases will pass through the tube and may be ignited at the other end, as shown in Fig. 13. In the middle or luminous cone an imperfect combustion takes place.

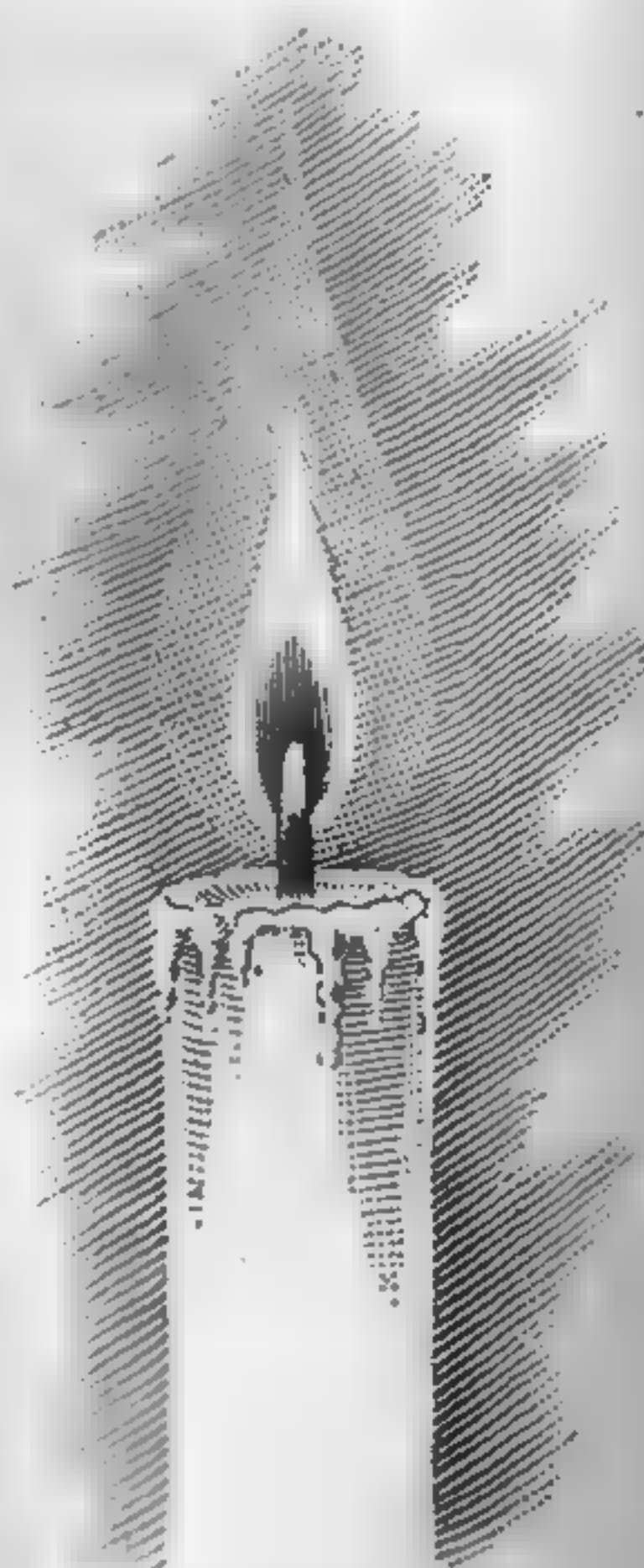


FIG. 12

The gases break down, some burning completely, and the free carbon is heated to incandescence and gives luminosity to this part of the flame. The carbon is not burned, owing to the lack of sufficient oxygen for its combustion. The presence of free carbon in this cone is shown by depressing a porcelain plate on the cone, when a black film of soot will be deposited. The outer cone, or mantle, of the flame is very feebly luminous.

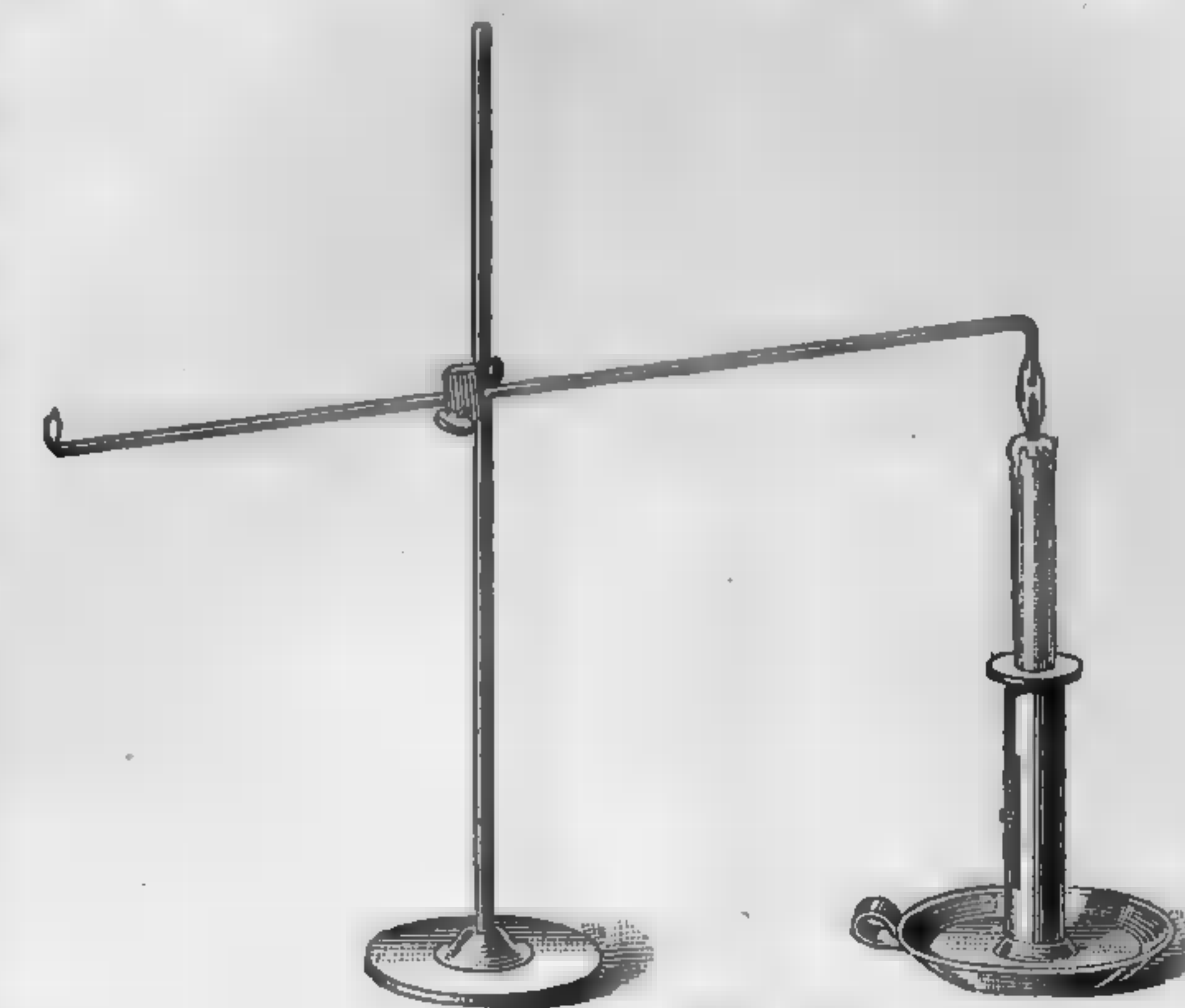


FIG. 13

In this cone, which is surrounded by air, the separated carbon burns completely, and the cone is termed the *cone of perfect combustion*. The last cone, or rather the bright-blue cup surrounding the base of the flame, is formed by the perfect combustion of a small portion of the hydrocarbons. Owing to the plentiful supply of air at this point there is no separation of carbon.

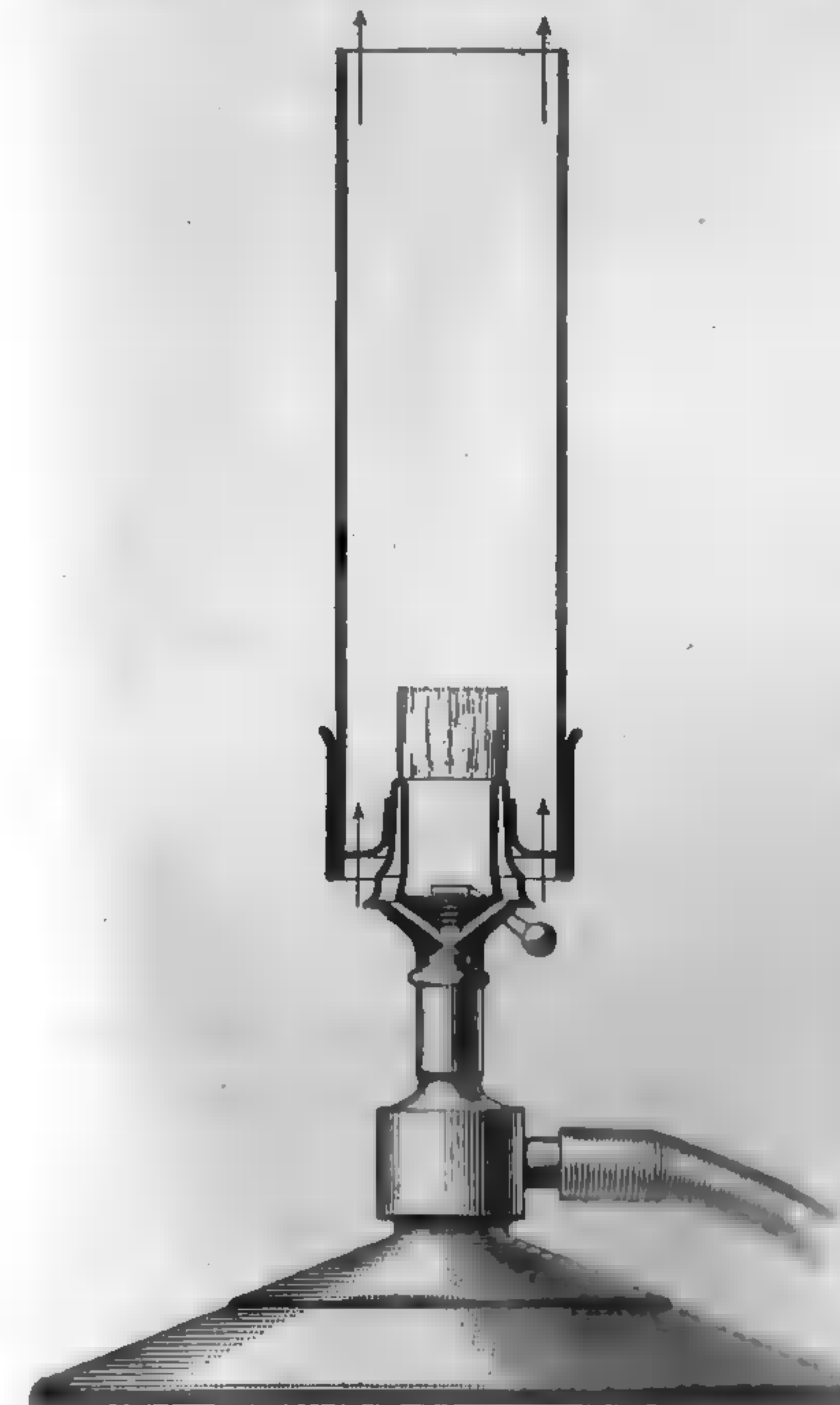


FIG. 14

43. As has been stated, all gas flames possess an identical structure, and by proper attention to the supply of air a flame fitted for either heating or illuminating can be obtained as desired.

For illuminating purposes the best results are obtained by what is known as the *Argand burner*, which is shown in Fig. 14.

Air is admitted to the gaseous center of a ring-shaped flame, and the use of a chimney to produce a draft insures great brilliancy and steadiness of the flame. A later and probably more brilliant flame for illuminating purposes employs the incandescence obtained by heating an incombustible solid, usually one of the rare earths.

An excellent burner for heating purposes is *Bunsen's burner*, shown in Fig. 15. This consists of a gas tube *a* projecting into the large mixing tube *b*.

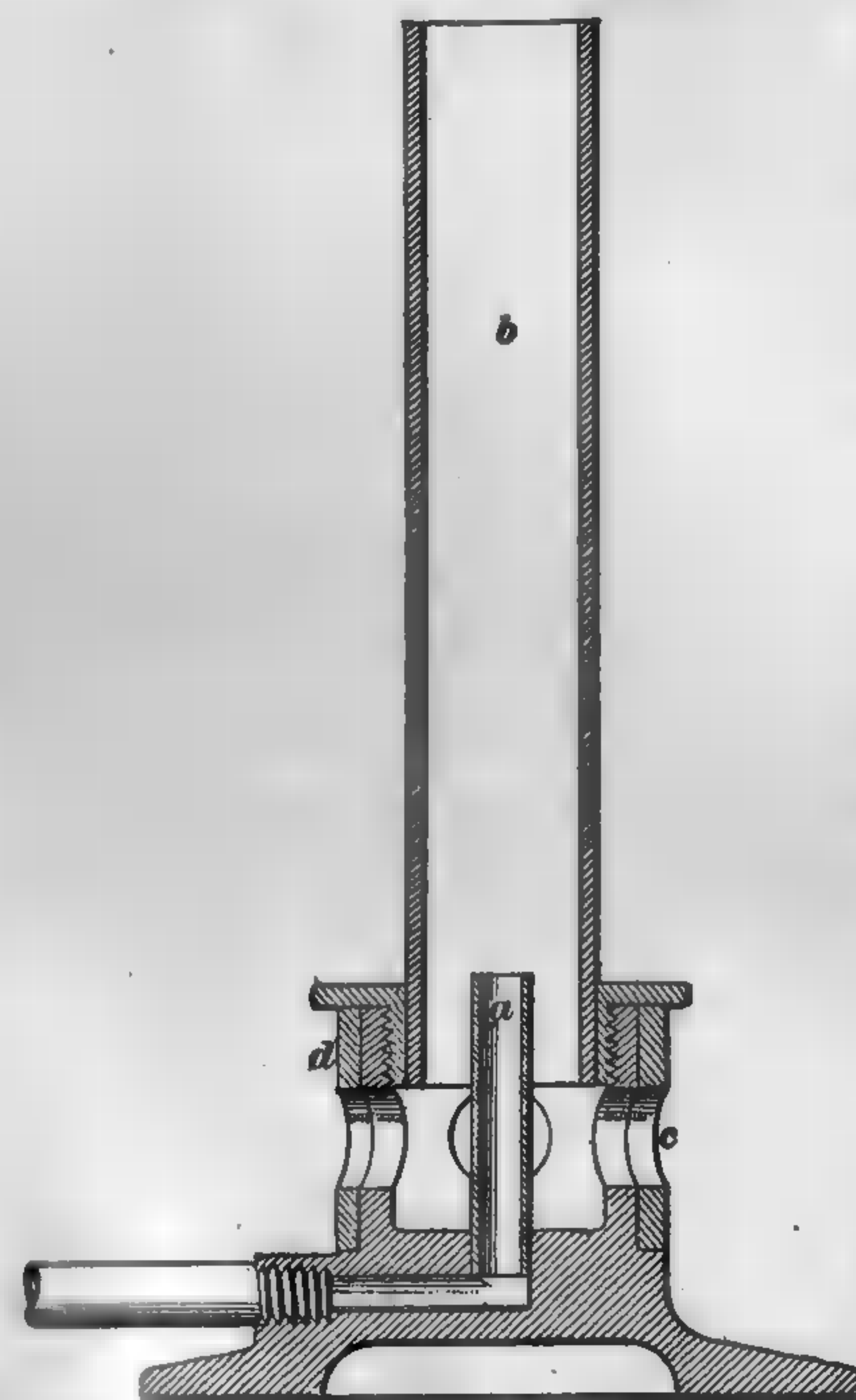


FIG. 15

Air enters through the openings *c* at the base of the burner, which are closed or opened by the collar *d*, thus regulating the supply of air. When a good supply of gas is turned on, a quantity of air, about double the volume of gas, is drawn in through the openings *c*, and the flame obtained by igniting the gaseous mixture at the orifice of the wide tube *b* affords an intense heat but no luminosity. If the air holes are closed a luminous flame is at once produced. The non-luminous flame contains an excess of oxygen and is used for oxidizing purposes, hence is known as an *oxidizing flame*. The *luminous*, or *reducing flame*, is, as its name implies, reducing in its action, the glowing carbon in it abstracting oxygen from many substances containing it.

The luminous flame may be converted into a non-luminous flame possessing considerable heating powers by blowing a current of air from a jet into the flame. The instrument used for this purpose is termed a *blowpipe*.

When a good supply of gas is turned on, a quantity of air, about double the volume of gas, is drawn in through the openings *c*, and the flame obtained by igniting the gaseous mixture at the orifice of the wide tube *b* affords an intense heat but no luminosity. If the air holes are closed a luminous flame is at once produced. The non-luminous flame contains an excess of oxygen and is used for oxidizing purposes, hence

44. The Miner's Safety Lamp.—Davy discovered the fact that flame, if cooled below a certain point, is extinguished; hence, that no flame can be propagated through a cold, fine metal tube.

EXPERIMENT.—Wire gauze, being a collection of small, short tubes, will, consequently, not allow the passage of flame, and, when pressed on a gas flame, will depress it in the same way as if it were a solid plate. If the gauze is held 2 inches above the jet, the gas may be lighted above the gauze, but the flame will not pass through to the jet. With two pieces of gauze, the gas may be made to burn between them, but neither above the upper nor below the lower; or, the gas may be made to burn above and below, but not between them.

The *miner's safety lamp*, generally known as *Davy's safety lamp*, is based on this discovery. It is represented in section in Fig. 16, and consists of a metallic lamp, the wick of which is surrounded with wire gauze, enclosed in a frame, by which the whole may be suspended. The explosive mixture of air with the gases developed in the mines can, of course, enter the gauze and burn within the gauze enclosure, but the flame cannot pass outwards through the gauze, since it is cooled, and consequently extinguished; hence, such a lamp prevents the explosion of these dangerous gases.

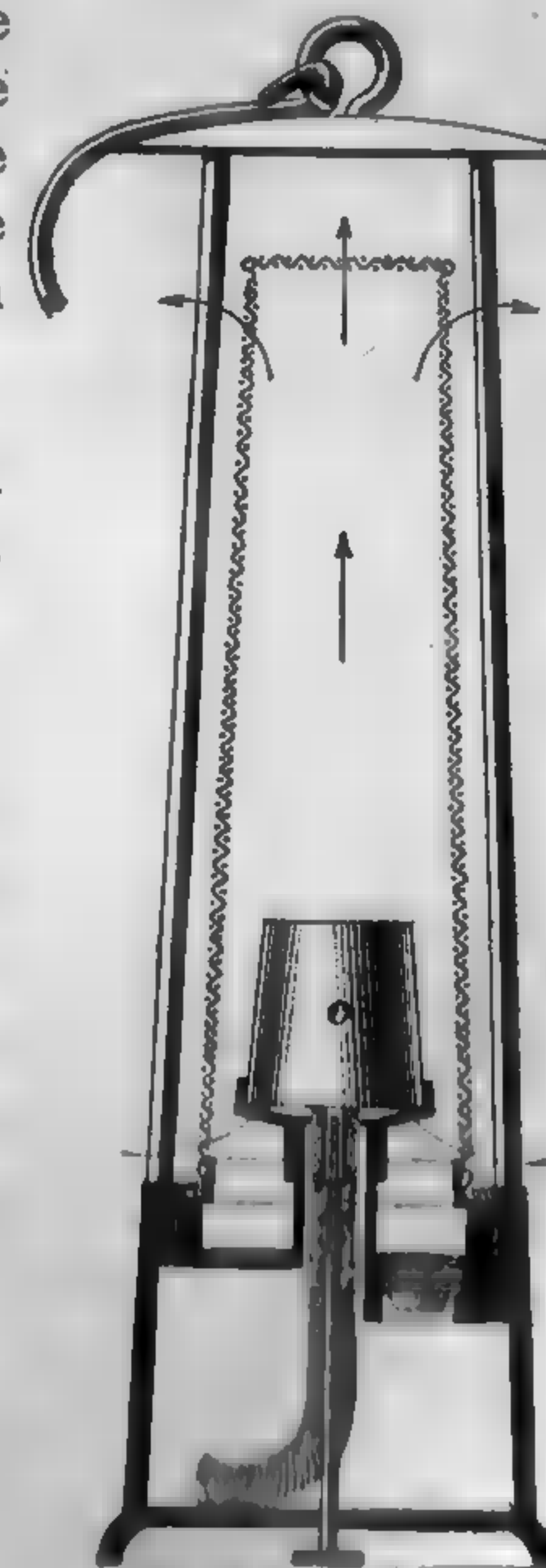


FIG. 16

45. Products of Combustion.—The products of combustion may be divided into two classes, namely, the *physical products*, such as light and heat, for the sake of which combustion is generally produced; and the *chemical products* that are to be conveyed away; these must be carbon dioxide and water, since the combustibles are composed of carbon and hydrogen.

EXPERIMENT.—That water is one of the chemical products of combustion may be readily proved by holding a cold, perfectly dry, bell jar over a candle flame; it will be noticed that it is at once bedewed with moisture.

If a little lime water is shaken in the jar, it will become milky, thus proving the presence of carbon dioxide. The same is true of respiration; a full breath blown through a glass tube into lime water will make it entirely white.

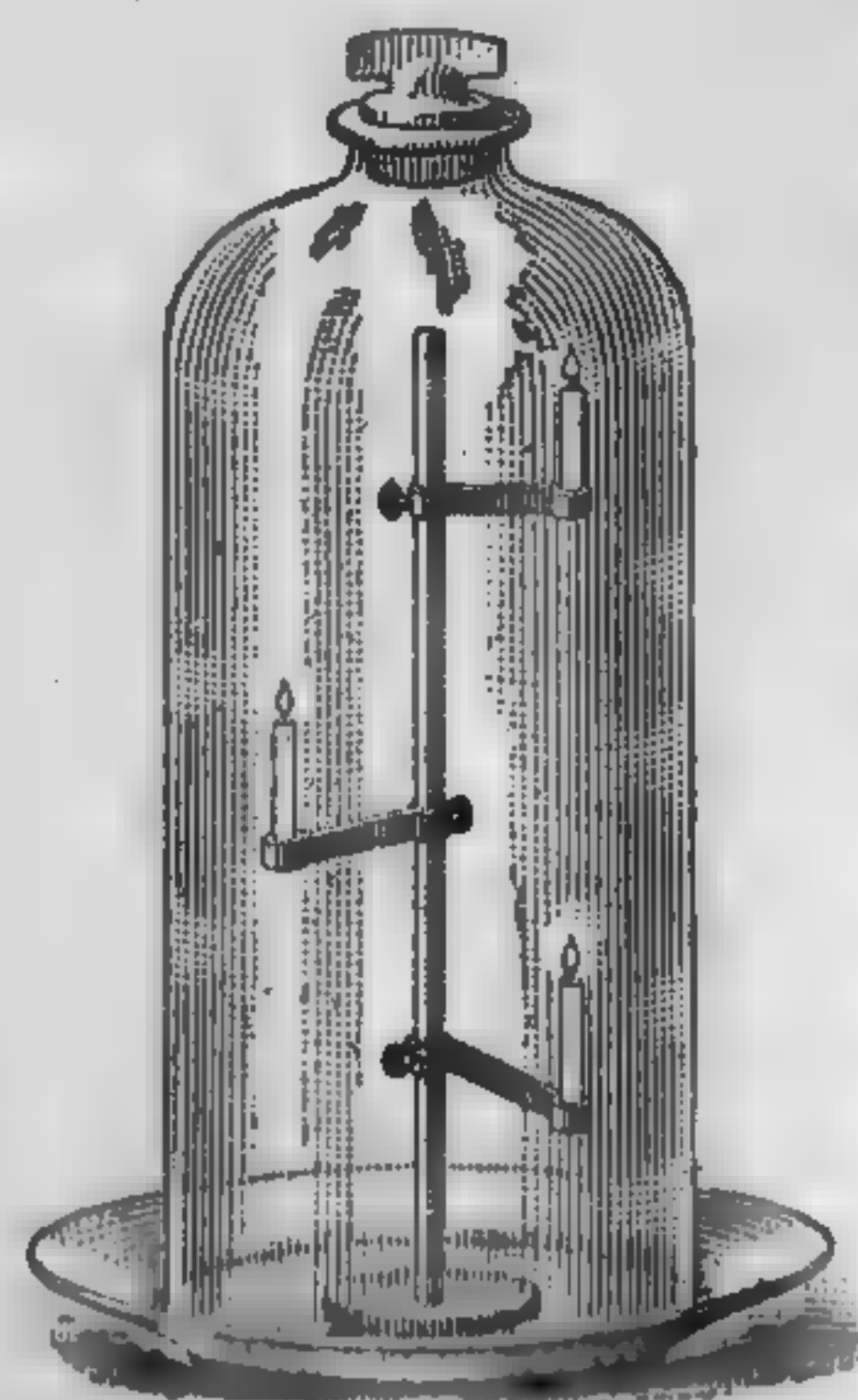


FIG. 17

46. **Ventilation.**—Pure air may be defined as air composed of nitrogen, oxygen, and carbon dioxide (about 3 parts in 10,000), together with some water vapor, ammonia, and hydrogen dioxide, and nothing of an injurious nature. The most common cause of the contamination of air is the breathing of human beings in rooms to which there is an inadequate supply of fresh air. The air issuing from the lungs of a human being at each expiration contains from 3 to 4 parts of carbon dioxide in each 100 parts of air. This amount could not be breathed again without danger, hence the necessity for a continued supply of fresh air to dilute the carbon dioxide sufficiently to render it no longer dangerous. The natural processes of respiration tend to raise the temperature of the air, thus causing it to expand and diminish its specific gravity, and causing it to ascend, and give place for fresh air. In order to remove the vitiated air a means of escape near the ceiling should be provided.

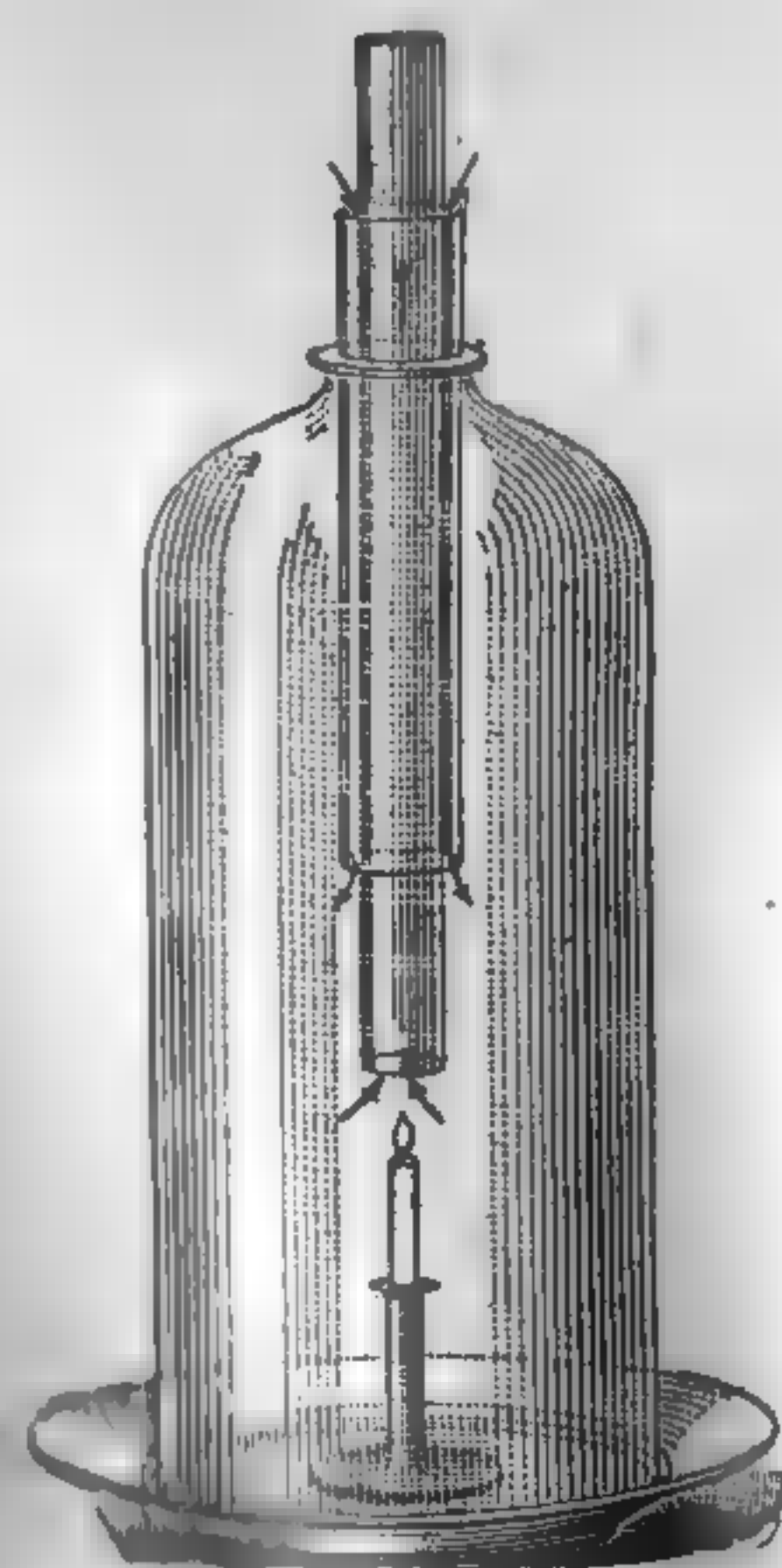


FIG. 19

47. The principles of ventilation are usually illustrated by means of the apparatus shown in Figs. 17, 18, and 19. If lighted candles held at different heights are covered with a bell jar as in Fig. 17, the carbon dioxide formed by the burning candles, being heated, will accumulate in the upper

part of the bell jar and will gradually extinguish the candles, the upper one being extinguished first. If, however, a glass tube is placed in the neck of the bell jar, so that the inner end is just slightly above the lower candle, as shown in Fig. 18, both candles will be extinguished. If the bell jar is raised slightly so as to allow air to enter, the upper candle will go out and the lower one will continue to burn. The air entering below will replace the carbon dioxide formed, which will pass out through the tube. The same result can be accomplished by placing two tubes, one within the other, in the neck of the bell jar, Fig. 19. The products of combustion escape through the center tube, and fresh air enters through the space between the tubes, and the candle continues to burn.

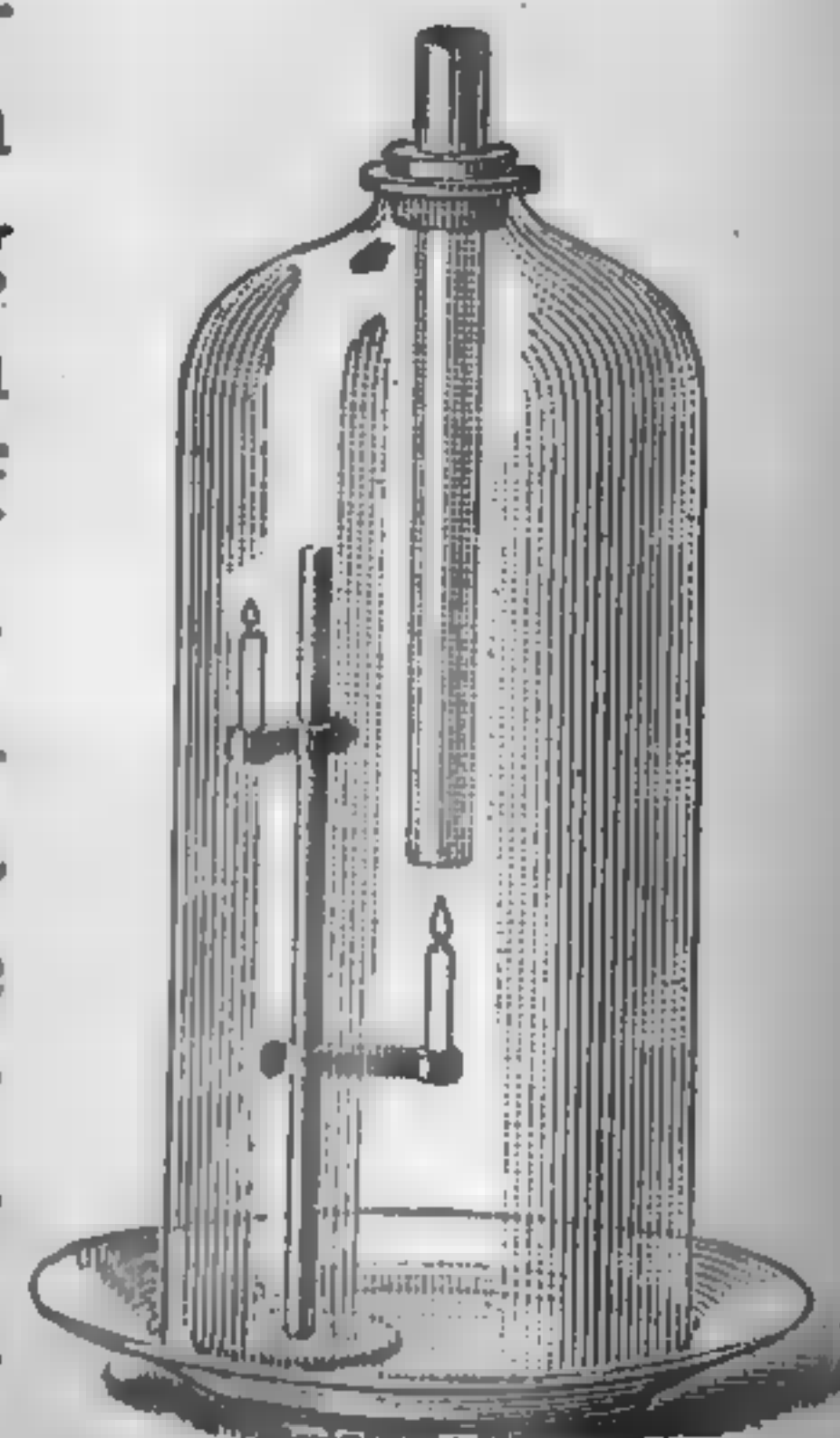


FIG. 18

part of the bell jar and will gradually extinguish the candles, the upper one being extinguished first. If, however, a glass tube is placed in the neck of the bell jar, so that the inner end is just slightly above the lower candle, as shown in Fig. 18, both candles will be extinguished. If the bell jar is raised slightly so as to allow air to enter, the upper candle will go out and the lower one will continue to burn. The air entering below will replace the carbon dioxide formed, which will pass out through the tube. The same result can be accomplished by placing two tubes, one within the other, in the neck of the bell jar, Fig. 19. The products of combustion escape through the center tube, and fresh air enters through the space between the tubes, and the candle continues to burn.

CARBON DISULPHIDE

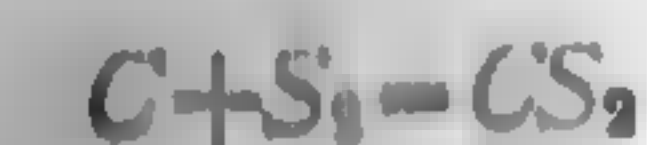
Formula CS_2 . Density 38.07. Molecular weight 76.14.

48. **History and Preparation.**—Carbon disulphide, also known as *carbon bisulphide*, was accidentally discovered by Lampadius in 1796. It is found in small quantities among the products of the destructive distillation of coal. It is formed,



FIG. 20

like the dioxide, by the direct union of its elements. It is prepared on a large scale by passing the vapor of sulphur over red-hot charcoal, the elements uniting according to the following equation:



Carbon disulphide may be prepared on a small scale in the laboratory by means of the apparatus shown in Fig. 20. The

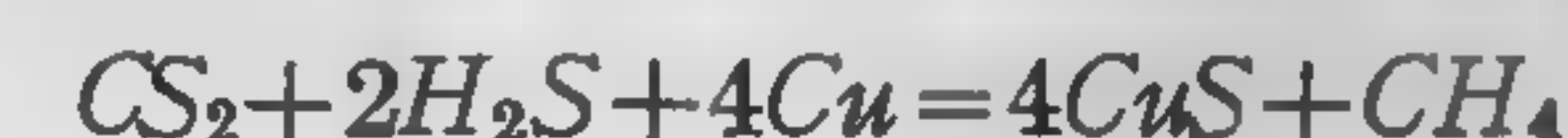
combustion tube, which should be about 2 feet long, is filled for about 3 inches from the sealed end with small pieces of sulphur; the rest of the tube is filled with small pieces of charcoal. The open end of the tube is connected with a glass tube dipping below the surface of water in a bottle placed in ice water. The charcoal is heated to redness first and then the part containing the sulphur is heated. The sulphur vapor passes over the red-hot charcoal, combines with the carbon, and is deposited under the water in the receiver. The excess of sulphur and the water are removed by distilling on a water bath.

On a large scale, an upright cast-iron cylinder from 10 to 12 feet long and about 2 feet in diameter, and provided with a lid to admit of charging with charcoal, is used. The cylinder has a hopper near the bottom for the purpose of introducing the sulphur. The whole is heated from below. The sulphur vaporizes, combines with the red-hot carbon, is condensed in a long iron tube, and collects under water in an iron basin. The impure material is then purified by distillation.

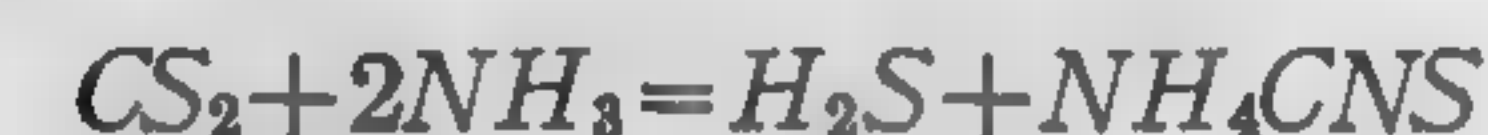
49. Properties.—Carbon disulphide is a colorless, mobile, brilliant, strongly refractive liquid that, when perfectly pure, possesses an agreeable ethereal odor, resembling that of chloroform. Its specific gravity is 1.29. It solidifies at -116°C. , and melts again at -110°C. ; it boils at 47°C. , yielding a dense vapor. It is very volatile, evaporating rapidly in the air, producing great cold. It is readily inflammable, taking fire in the air at 150°C. and burning with a blue flame, producing carbon and sulphur dioxide by its decomposition. A mixture of carbon-disulphide vapor and oxygen forms an explosive mixture, even when the mixture is thoroughly dry. The vapor of carbon disulphide is poisonous when inhaled in large quantities, its effects showing symptoms very similar to those of hydrogen sulphide poisoning. Carbon-disulphide vapor burns in nitric oxide with an intensely brilliant blue flame. Carbon disulphide is only slightly soluble in water, but is miscible with alcohol and ether in all proportions.

Carbon disulphide is used in the arts as a solvent for caoutchouc, and as a solvent for oils and fats, and frequently it

is employed for extracting the essential oils that contain the perfumes of roses, lavender, jasmine, etc. It also dissolves sulphur, phosphorus, and iodine, and is used to determine the moisture in commercial iodine. It is also frequently used as a starting point in the synthetic preparation of the hydrocarbons, because if mixed with hydrogen sulphide and passed over copper filings heated to redness, methane is produced, thus:



When carbon disulphide is dissolved in alcohol and is acted on by ammonia with the aid of heat, ammonium sulphocyanide is formed according to the equation:



50. Carbon oxysulphide, COS, is formed when a mixture of carbon monoxide and sulphur vapor is passed through a moderately heated tube or is subjected to the action of electric sparks. It is usually prepared by gently heating potassium sulphocyanide with dilute acids. The potassium sulphocyanide is first broken up into sulphocyanic acid:



and the sulphocyanic acid is then decomposed by the water of dilution, thus:



In practice, however, sufficient sulphuric acid is added to unite with the ammonia gas and form ammonium sulphate, thus:



Carbon oxysulphide is a colorless gas with a peculiar odor somewhat resembling that of carbon disulphide. It has a specific gravity of 2.11, and is very inflammable, burning with a bright blue flame to carbon dioxide and sulphur dioxide. It is rapidly absorbed by aqueous or alcoholic solutions of caustic potash, yielding the carbonate and sulphide of potassium, for instance:

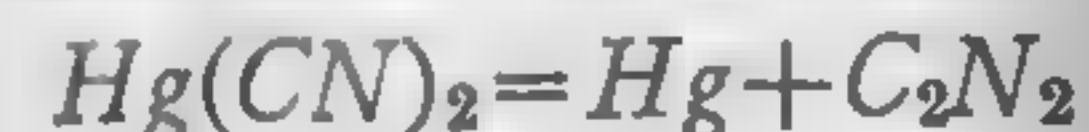


CYANOGEN

Formula C_2N_2 . Density 2.601. Molecular weight 52.02.

51. History and Preparation.—Cyanogen was discovered by Gay-Lussac in 1815; being the first compound radical isolated, its discovery marks an era in the science of theoretical chemistry, and, to a still greater extent, in that of organic chemistry. Its name is derived from a Greek word meaning *blue*, in allusion to its being an important constituent

of the well-known pigment, *Prussian blue*, then known as *prussiate of iron*, from which Gay-Lussac first obtained it. Cyanogen can be obtained by heating the cyanide of gold, silver, or mercury:



EXPERIMENT.—Instead of using the somewhat rare and rather expensive mercuric cyanide, a mixture of 2 parts of thoroughly dried potassium ferrocyanide and 3 parts of mercuric



FIG. 21

chloride may be used. The mixture is placed in a flask of hard glass on a sand bath, Fig. 21, and heated intensely. The gas as it is evolved may be collected by displacement, its strong odor indicating when the jar is filled.

Cyanogen is also prepared (as in the experiment) by heating cyanides with mercuric chloride, distilling ammonium oxalate with phosphorus pentachloride, and by adding a concentrated solution of potassium cyanide to a solution of copper sulphate and heating the mixture. Cuprous cyanide separates out and cyanogen is evolved.

52. Properties.—Cyanogen is a colorless gas, exceedingly poisonous, possessing a strong odor of bitter almonds. Its

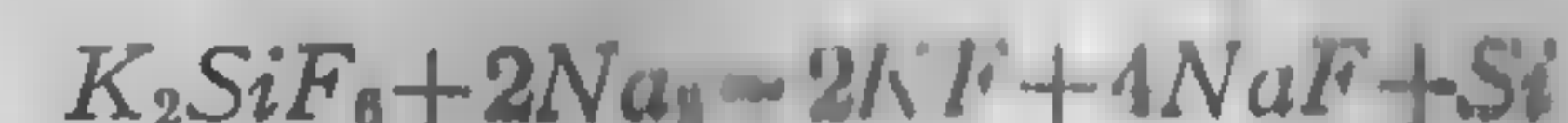
specific gravity is 1.806. It may be easily condensed by a pressure of 4 atmospheres or at a temperature of $-25^{\circ}C$. to a colorless, highly refractive liquid, which has a specific gravity of .866 and freezes at $-34^{\circ}C$. to a transparent, icelike solid. Water dissolves four and one-half times its own volume of cyanogen, and alcohol twenty times its own volume of the gas. On contact with flame, cyanogen readily takes fire, and burns with a characteristic pink flame edged with green, yielding carbon dioxide and nitrogen. Free, or molecular, cyanogen is composed of two of the cyanogen radicals, CN , $(CN)_2$, being analogous to Cl_2 . Moreover, the cyanogen radical acts precisely like an elemental monad, forming compounds corresponding to the chlorides, thus: Potassium chloride, KCl ; hydrochloric acid, HCl ; hypochlorous acid, $HClO$; potassium cyanide, KCN ; hydrocyanic acid, HCN ; cyanic acid, $HCNO$.

SILICON

Symbol Si . Atomic weight 28.3. Valence IV. Specific gravity 2.49.

53. History and Occurrence.—Silicon was first obtained pure by Berzelius in 1825. It does not occur free in nature, but is found abundantly in combination with oxygen, forming such well-known substances as quartz and flint. In combination with oxygen, as well as with aluminum, potassium, and various other metals, it constitutes a large portion of the rock formations that compose the solid crust of the earth.

54. Preparation and Properties.—Silicon may be obtained by the action of sodium on potassium fluosilicate:



The silicon thus obtained is a brown powder (*amorphous silicon*) that resists the action of all acids, except hydrofluoric, which it decomposes, forming silicon tetrafluoride and evolving hydrogen:



It may also be dissolved by a solution of potassium hydroxide, with the evolution of hydrogen, and the formation of

potassium silicate. Though silicon burns brilliantly when heated in oxygen, it does not burn completely, owing to the fact that it becomes coated with silicon dioxide, which is fused by the intense heat of the combustion. When heated with the blowpipe on platinum foil, it eats a hole through the metal, with which it forms the fusible platinum silicide.

If potassium fluosilicate is fused with aluminum, a portion of the latter combines with the fluorine, while the remainder combines with the silicon, forming aluminum silicide. By boiling this with hydrochloric acid and then with hydrofluoric acid, the aluminum is extracted and crystalline scales of silicon, possessing a metallic luster, resembling that of black lead, are left. These crystalline scales are known as *graphitoid silicon*. In this shape, silicon does not burn in oxygen, nor is it then soluble in hydrofluoric acid; a mixture of nitric and hydrofluoric acid, however, is capable of dissolving it. Though amorphous silicon is a non-conductor of electricity, the crystalline variety, like graphite, readily conducts it. The amorphous variety may, through an extremely intense heat, be transformed into the incombustible and insoluble form. It seems appropriate to remark that the combustibility of amorphous carbon (charcoal) is also diminished to a considerable extent after exposure to a high temperature.

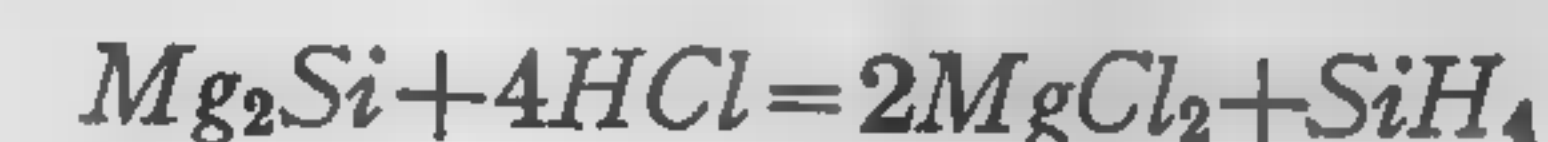
Silicon is capable of being fused at a temperature somewhat above the melting point of cast iron; on cooling, it forms a brilliant metallic-looking mass, which may be obtained by certain processes, crystallized in octahedrons, whose hardness is so great that they scratch glass like diamond.

In their chemical relations to other substances, a considerable analogy exists between silicon and carbon. Silicon, however, is capable of displacing carbon; as, for instance, if potassium carbonate is fused with silicon, the former is dissolved, forming potassium silicate, and carbon is separated. Silicon further resembles carbon in its disposition to unite with metals, and to form compounds that retain their metallic luster; it unites directly with zinc, platinum, and aluminum, forming compounds that resemble metallic alloys. Nitrogen enters into combination with silicon directly at high temperature.

SILICON HYDRIDE

Formula SiH_4 . *Molecular weight* 32.33.

55. History and Preparation.—Silicon hydride was discovered by Wöhler and Buff in 1857, and obtained in a pure state in 1867 by Friedel and Ladenburg. It is generally prepared by decomposing magnesium silicide by hydrochloric acid:



EXPERIMENT.—The first step in this experiment is to prepare magnesium silicide. For this purpose 40 parts of fused magnesium chloride, 35 parts of dried sodium fluosilicate, 10 parts of sodium chloride, and 20 parts of sodium cut in small pieces, are thoroughly mixed together and thrown into a red-hot Hessian crucible, which, after being covered with a lid, is further heated until the sodium ceases to burn. When cold, a dark layer of the impure silicide will be found at the bottom; this is detached and may be preserved in a small, tightly stoppered bottle.

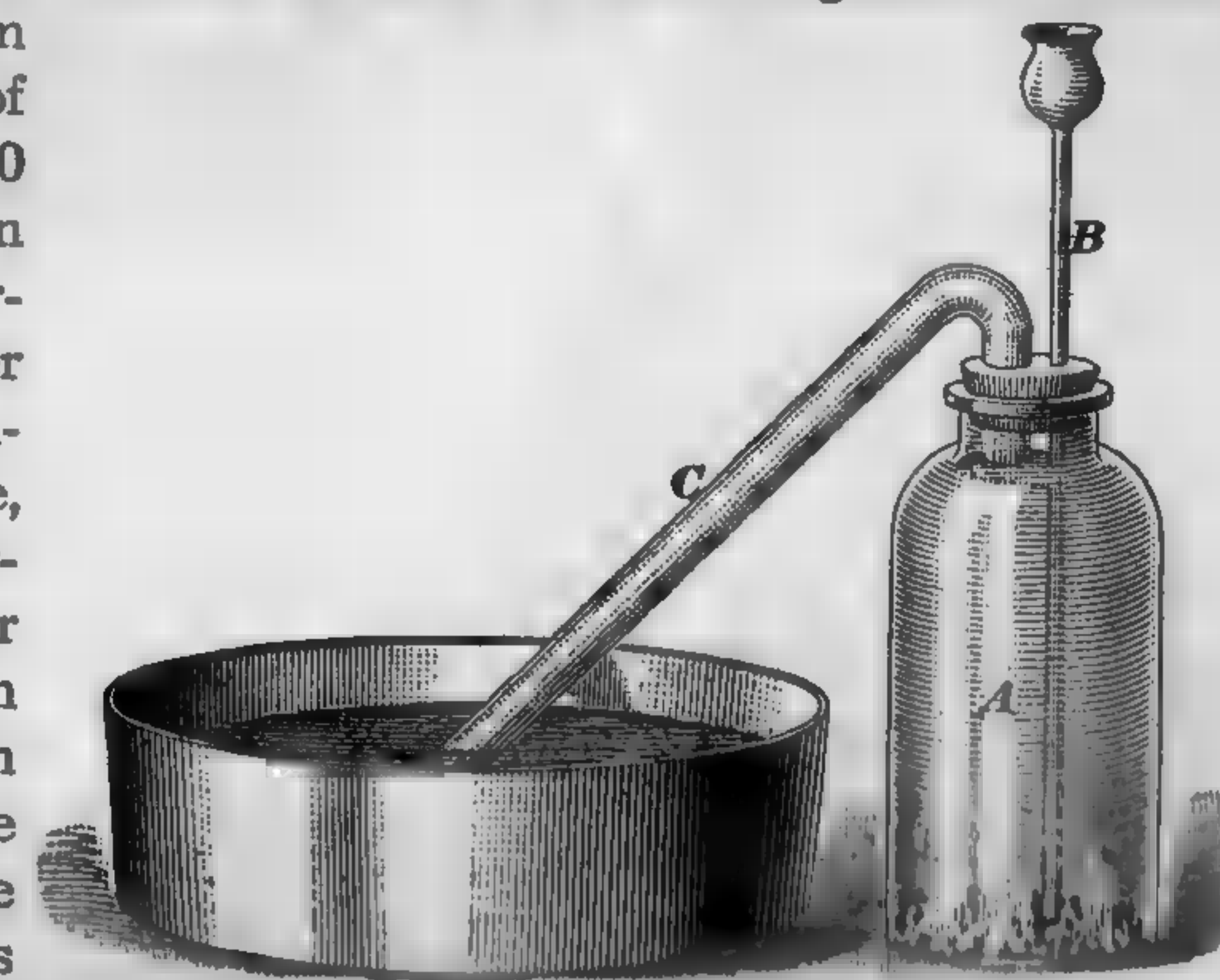


FIG. 22

To prepare silicon hydride, the coarsely pulverized slag is placed in a wide-mouthed bottle *A*, Fig. 22, through the stopper of which passes a funnel tube *B* to the bottom of the bottle, and a wide delivery tube *C*, for the escape of the gas. The bottle is then filled with cold water, which, however, must have been recently boiled in order to expel its air, and placed by the pneumatic trough, as shown in the illustration. Upon pouring concentrated hydrochloric acid down the funnel, being very careful that it does not carry any air bubbles with it, silicon-hydride gas is evolved and may be collected for use.

56. Properties.—Silicon hydride is a colorless gas, which at -1°C . under a pressure of 70 atmospheres is condensed into a liquid. It is insoluble in water. When mixed with hydrogen, it is spontaneously inflammable in air, yielding

white clouds of silicon dioxide. Burned from a jet, the gas gives a brilliant white flame that deposits a layer of brown silicon upon a disk or plate of porcelain held in it. When the tube conveying the gas is heated, a mirror-like deposit of silicon is formed within the tube. Passed into cupric sulphate or silver nitrate, it precipitates cupric and silver silicide, respectively. Its composition can easily be proved by decomposing it with potassium hydroxide:



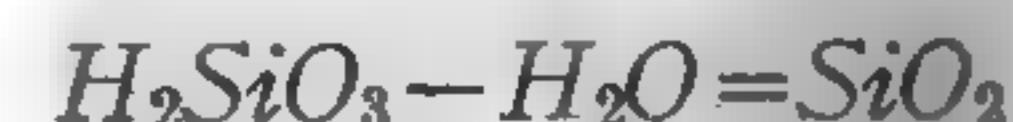
It is readily seen from the equation that 1 volume of the gas with potassium hydroxide yields 4 volumes of hydrogen, and that one-half of this hydrogen comes from the silicon hydride; each molecule must then contain 2 molecules of hydrogen, or 4 atoms.

SILICON DIOXIDE

Formula SiO_2 . Molecular weight 60.3.

57. Occurrence.—The only oxide of silicon known, silicon dioxide, or *silica*, is found widely distributed in nature as quartz, opal, flint, sand, etc. It occurs also in combination with bases in the form of silicates, as asbestos, mica, soapstone, cement, glass, etc. Its purest form is the transparent and colorless variety known as *quartz*, which crystallizes in the hexagonal system and has a specific gravity of 2.6, and a hardness of 7. When colored a delicate purple, the crystals are known as *amethysts*. When its transparency and crystalline structure are lost and it is colored with iron oxide, it becomes *chalcedony* and *carnelian*.

58. Preparation and Properties.—Silica may be prepared either by the oxidation of silicon, as when it burns in the air, or by the dehydration of silicic acid:



Silicon dioxide, in the form in which it is usually obtained, is a white amorphous powder, though in nature it frequently occurs in the form of hexagonal prisms. It has a specific

gravity of 2.6, is so hard as to scratch glass, and is fusible only by means of the oxyhydrogen blowpipe. It is insoluble in water and all acids, but is soluble in the fixed alkalies, and is decomposed by hydrofluoric acid, forming silicon fluoride and water.

When a portion of the sodium hydroxide solution of silica, sodium silicate or *water glass*, is treated with a few drops of hydrochloric acid, gelatinous silicic acid will separate out. If, however, a portion is quickly poured into an excess of dilute hydrochloric acid, the silicic acid will remain dissolved in the water, together with the sodium chloride formed. The sodium chloride can be separated from the silicic acid only by dialysis.

59. Dialysis, from the Greek word meaning *to rend asunder*, is the separation of dissolved substances from one another by taking advantage of the different rates at which they pass through moist *diaphragms*. Substances which crystallize (*crystalloids*) and mineral acids pass through diaphragms much more rapidly than do amorphous substances (*colloids*).

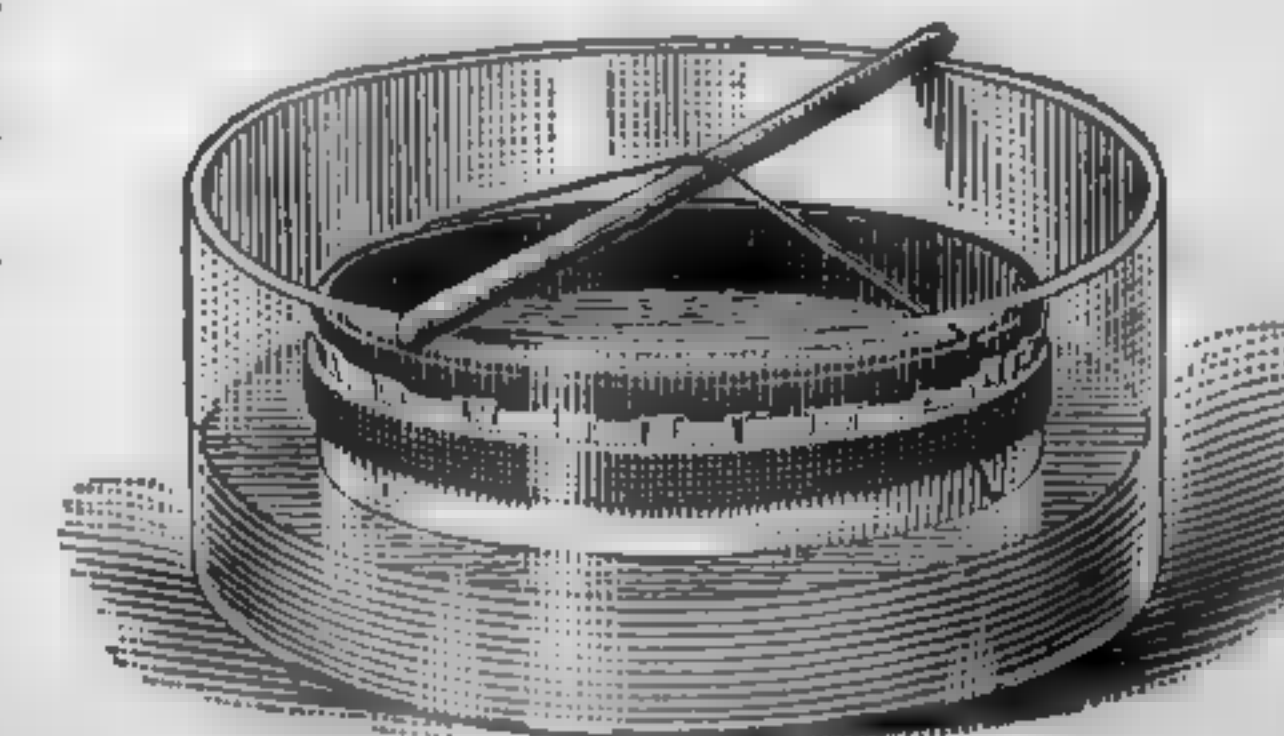


FIG. 23

A solution containing sodium chloride and silicic acid poured on a parchment paper, which is not pervious to water, although readily moistened by it, will have the sodium chloride separated by its passing through the parchment paper while the silicic acid will remain on the paper.

The ordinary form of dialyzer met with in laboratories consists of a parchment paper stretched over a hard-rubber ring and held in position by a concentric ring. It is suspended on a surface of water and the solution to be dialyzed is poured on it. Fig. 23 illustrates a dialyzer such as described. The solution of silicon dioxide in a fixed alkali hydroxide is really *orthosilicic acid*, H_4SiO_4 . It is only feebly acid to blue litmus paper and has no perceptible sour taste. When the solution is evaporated in vacuum over sulphuric acid, it forms a transparent lustrous glass containing 78 per cent. of silicon dioxide, and is *metasilicic acid*, H_2SiO_3 .

60. Natural crystallized silica is not soluble in boiling solutions of the alkalis, nor is it soluble in any of the acids with the exception of hydrofluoric acid. The amorphous variety, on the other hand, is readily soluble in boiling alkalis. Thus, silica is found to exist in two modifications, and is dimorphous. A crystal of quartz may be heated to a bright redness without change; but, if powdered previous to being heated its specific gravity changes from 2.6 to 2.4, and it becomes soluble in boiling alkalis. In other words, by fine grinding and heating the crystalline modification becomes converted into the amorphous.

61. Silicates.—Owing to the weak acid properties of silicic acid, it is a difficult matter to determine the proportion of any base that is required to react with the acid in order to form a chemical neutral salt. The acid does not destroy the action of the alkalis on test papers, and the proportion of carbon dioxide expelled when the acid is heated with an alkaline carbonate varies so greatly that this also offers no means of determining the proportion.

When silica is heated with sodium hydroxide it is found that 60 parts of silica expel 36 parts of water no matter how much sodium hydroxide is used, and the same is true if barium hydroxide is used in place of sodium hydroxide. The formula SiO_2 represents 60 parts by weight of silica and 36 parts represent two molecules of water. It is also known that several of the crystallized mineral silicates contain a quantity of metal equivalent to 4 atoms of hydrogen. Hence, silicic acid is represented as a tetrabasic acid containing four replaceable hydrogen atoms.

By far the greatest number of minerals are silicates. Clays are aluminum silicates, meerschaum and talc are silicates of magnesium, feldspar is a silicate of aluminum and potassium, the various glasses are silicates of sodium, potassium, lead, calcium, etc. The majority of the silicates are represented as derivatives of metasilicic acid and polysilicic acids of the general formula $n\text{H}_2\text{O} \cdot \text{SiO}_2$.

62. Uses of Silica.—Silica is largely employed in all its various forms. Rock crystal is used for the manufacture of

ornaments, etc. Chalcedony, onyx, and opal are sought for by the engraver and lapidary. Agate, which is very hard, is used for the manufacture of mortars, etc. Sandstone serves for building purposes and for grindstones; sand, for mortars, the manufacture of glass, pottery, etc.

SILICON TETRACHLORIDE

Formula SiCl_4 . Molecular weight 170.14.

63. Preparation and Properties.—Silicon tetrachloride is formed when silicon is heated to dull redness in a current of chlorine, or when the latter gas is passed over an incandescent mixture of charcoal and silica, according to the equation:



Silica, lampblack, and oil are thoroughly mixed into a stiff paste, which is made into little balls that are placed in a crucible, the cover of which is then luted, and the whole is heated to redness in a furnace. When cool, the balls are introduced into a porcelain tube or a clay retort, which is heated to bright redness in a furnace while a current of carefully dried chlorine is passed through. The silicon tetrachloride and the carbon monoxide formed are passed through two U tubes surrounded by a freezing mixture, by which means the silicon tetrachloride is condensed.

Silicon tetrachloride is a colorless, heavy liquid, specific gravity 1.52, and is volatile. Its boiling point is 59°C . and it fumes readily when exposed to air, the moisture of which decomposes it, yielding hydrochloric acid and silicic acid according to the equation:



64. Silicon hexachloride, Si_2Cl_6 , is formed when silicon tetrachloride is passed over silicon heated to whiteness in a porcelain tube. It is a colorless liquid, specific gravity 1.58, that solidifies at -1°C . and boils at 140°C . Its vapor density is 9.7. It fumes strongly in the air, and takes fire when heated.

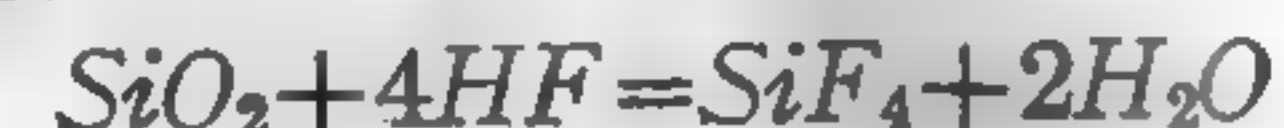
SILICON, IODINE, AND BROMINE

65. With bromine and iodine, silicon forms also the compounds SiBr_4 , Si_2Br_6 , Si_2Br_8 , SiI_4 , and Si_2I_6 , which are analogous in composition to the chlorine compounds. Silicon tetrabromide, SiBr_4 , is a colorless, heavy liquid that boils at 151°C . and solidifies to a crystalline mass at -13°C . Silicon hexabromide, Si_2Br_6 , forms large crystalline tablets, melts when heated, and distils without decomposition at 240°C . Silicon tetraiodide, SiI_4 , is obtained by direct combination; it melts at 120.5°C . and boils at 290°C .; it takes fire when heated in the air and burns with a reddish flame; it is decomposed by water into hydriodic and silicic acid. Silicon hexiodide, Si_2I_6 , is obtained when silicon tetraiodide is heated at 280°C . with finely divided silver. It crystallizes from carbon disulphide in beautiful, colorless, hexagonal prisms or rhombohedrons, which, on exposure to moist air, are converted into a white mass, with the formation of silicic and hydriodic acid. Subjected to heat, silicon hexiodide melts and is decomposed. Ice-cold water decomposes it, with the formation of a white substance, $\text{H}_2\text{Si}_2\text{O}_4$, known as a disilicic acid. This compound is decomposed by weak bases into hydrogen and silica.

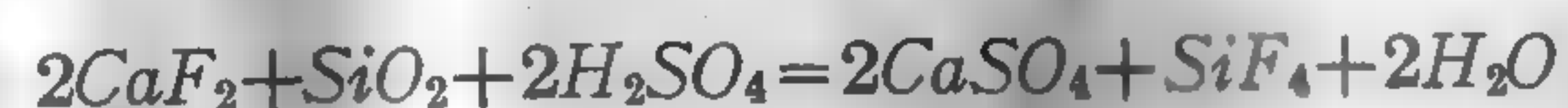
SILICON TETRAFLUORIDE

Formula SiF_4 . Molecular weight 104.3.

66. Silicon tetrafluoride is formed when hydrofluoric acid acts on silica, thus:

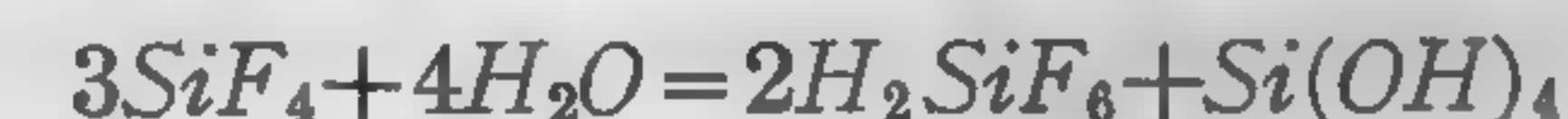


It is ordinarily prepared by heating a mixture of powdered glass or white sand and fluorspar with concentrated sulphuric acid. It may be formed also by a direct union of the elements. The reaction showing the formation of silicon tetrafluoride from fluorspar, sand, and sulphuric acid is:



Silicon tetrafluoride is a colorless, fuming, pungent gas that condenses to a colorless liquid under a pressure of 30 atmos-

pheres, and solidifies at -97°C . It melts at -77°C ., forming a transparent mobile liquid, which boils at -65°C . The gas resembles hydrofluoric acid in appearance; but, if a moistened glass rod is exposed to the gas the wet surface quickly becomes coated with a white film of silica. This crust is formed by the decomposition of the tetrafluoride by the water on the rod, thus:



67. Fluosilicic acid, H_2SiF_6 , is formed by passing silicon tetrafluoride into water, as already stated. As the silicic acid separates in a gelatinous mass that would stop the opening of the gas delivery tube, the tube is made to dip into a little mercury underneath the water. To obtain the fluosilicic acid, the thick jelly is pressed through a linen filter, and the filtrate is concentrated at a low temperature. The saturated solution is a strongly acid, fuming liquid, which, on boiling, decomposes into silicon tetrafluoride and hydrofluoric acid.

SILICON AND SULPHUR

68. Silicon disulphide, SiS_2 , is formed when the vapor of carbon disulphide is passed over a white-hot mixture of silica and carbon. It crystallizes in long, white, silky needles that are decomposed into hydrogen sulphide and silica by water, and which burn in the air to silica and sulphur dioxide.

SILICON AND NITROGEN

69. A compound of silicon and nitrogen, *silicon nitride*, SiN , is obtained when silicon is heated to a high temperature in an atmosphere of nitrogen, and the products are treated successively with hydrofluoric acid and potassium hydroxide. It is a green infusible powder, which at a red heat is decomposed by potassium hydroxide, yielding potassium silicate, hydrogen, and ammonia.

SILICON AND CARBON

70. Silicon carbide, SiC , or *carborundum*, is prepared by heating a mixture of sand, coke, and salt in an electric furnace, carbon electrodes being used. It may be obtained pure by

fusing the requisite amounts of carbon and silicon in an electric furnace. The pure carbide forms colorless or blue transparent, tabular crystals whose specific gravity is 3.12. It is nearly as hard as the diamond, is not oxidized by oxygen at 1,000° C., and is not attacked by sulphur, fused potassium nitrate, nor any acids. Melted caustic alkalies, however, convert it into the carbonate and silicate of the alkali metal.

TITANIUM

Symbol Ti. Atomic weight 48.1. Valence, III and IV.

71. Occurrence and Preparation.—Titanium exists in *rutile*, *brookite*, and *anatase*, which constitute three varieties of titanium dioxide, TiO_2 , and with iron in titaniferous iron ores. Cubical copper-colored crystals of a nitrocyanide of titanium are frequently found in the cinders of blast furnaces in which titaniferous ores have been reduced.

Titanium may be obtained in the free state by decomposing potassium fluotitanate with potassium, also by heating the oxide with aluminum. It is a gray-white metal, specific gravity 4.87, with a brilliant white fracture, is harder than steel, but crumbles readily. When heated in the air it burns, and at 100° C. it decomposes water with evolution of hydrogen. It does not form a compound with hydrogen, but unites directly with nitrogen at high temperatures. It dissolves in hydrochloric acid forming the *hexachloride*, Ti_2Cl_6 .

72. Titanium and Oxygen.—Titanium forms three oxides, the dioxide, TiO_2 , the sesquioxide, Ti_2O_3 , and the peroxide, TiO_3 . *Titanium dioxide*, TiO_2 , is one of the principal forms in which titanium occurs in nature. To obtain pure titanium dioxide from the mineral, the natural oxide is fused with potassium carbonate, when potassium titanate, K_2TiO_3 , is formed. When a solution of this is treated with an acid the titanium is precipitated as hydroxide, the composition of which varies from normal titanic acid, $Ti(OH)_4$ or H_4TiO_4 , to dititanic acid, $H_2Ti_2O_5$; and when the hydroxide is ignited it yields titanium dioxide, in the form of a white, insoluble, infusible powder.

73. Halogen Compounds of Titanium.—*Titanium tetrachloride*, $TiCl_4$, is obtained by the direct union of the elements, when chlorine acts on titanium at a fairly high temperature, or it may be prepared by passing chlorine over a mixture of titanium dioxide and carbon. It is formed also by passing the vapor of chloroform over heated titanium dioxide. It is a colorless liquid that forms crystalline compounds with water, has a specific gravity of 1.76, fumes strongly in the air, boils at 136.4° C., and has a penetrating acid smell. By heating with water, it is decomposed into titanium dioxide and hydrochloric acid. The compound Ti_2Cl_6 is formed by acting on titanium with hydrochloric acid, and the compound Ti_2Cl_4 has also been obtained.

Titanium tetrafluoride, TiF_4 , may be prepared by adding sulphuric acid to a mixture of titanium dioxide and fluorspar, or by acting on titanium dioxide with hydrofluoric acid. When the tetrafluoride is treated with water it forms *fluotitanic acid*, H_2TiF_6 .

74. Titanium Salts.—The hydroxides of titanium ordinarily conduct themselves as acids, but toward the stronger acids they also act as feeble bases, forming a few salts, as examples of which may be mentioned *titanium sulphate*, $Ti(SO_4)_2$, and *titanyl sulphate*, $TiOSO_4$.

ZIRCONIUM

Symbol Zr. Atomic weight 90.0. Valence IV.

75. Occurrence and Preparation.—Zirconium is a rather rare element. It occurs in nature principally as the mineral *zircon*, which is a silicate having the formula $ZrSiO_4$. Zirconium is obtained free by heating potassium fluozirconate to a high temperature with aluminum. The fluozirconate is thus decomposed, yielding zirconium in a crystalline condition, somewhat resembling bismuth or antimony. Zirconium dissolves in hot concentrated hydrochloric acid. Free zirconium, like carbon, is known in three modifications. It

forms hard, steel-gray plates having a specific gravity of 4.1, oxidizes very slowly in the air, but burns in the oxyhydrogen flame.

76. Zirconium and Oxygen.—*Zirconium dioxide* may be obtained from zircon. Zirconic acid, $Zr(OH)_4$ or H_4ZrO_4 , is precipitated from acid solutions of zirconium by ammonia; when this precipitate is heated it loses water and yields the dioxide, ZrO_2 . Zirconium dioxide is a rather feeble acid oxide. When fused with sodium or potassium carbonate it replaces the carbon dioxide, forming the corresponding zirconate, K_2ZrO_3 . With the stronger acids, zirconium dioxide acts as a weak base, forming some salts, one of which, $Zr_3(SO_4)_2$, is of especial interest, as it appears to be derived from normal sulphuric acid, $S(OH)_6$ or H_6SO_6 .

77. Halogen Compounds of Zirconium.—*Zirconium tetrachloride*, $ZrCl_4$, is formed by dissolving the element in hot concentrated hydrochloric acid, or by the direct union of the elements, when chlorine acts on zirconium. It is more stable than silicon or titanium tetrachloride, and is only partly decomposed by the action of water, forming *zirconium oxychloride*, $ZrOCl_2$. This is due to the fact that zirconium acts both as an acid-forming and base-forming element.

Zirconium tetrafluoride is obtained by passing hydrochloric-acid gas over a mixture of finely powdered zircon and fluor-spar at a high temperature. It unites with fluorides of the metals, forming fluozirconates, which are analogous to fluosilicates and fluotitanates.

CERIUM

Symbol Ce. Atomic weight 140.25. Valence III and IV.

78. Occurrence and Preparation.—Cerium occurs in the mineral cerite and is obtained by the electrolysis of the chloride. It is prepared also by heating the dioxide with powdered magnesium. It is a gray, ductile, malleable, metal that does not change in dry air, but tarnishes in moist air. It melts at $623^\circ C.$, has a specific gravity of from 6.6 to 7, ignites

in the air more readily than does magnesium, and burns with extreme brilliancy. When scratched or rubbed with metal, the finely divided particles of cerium take fire. Alloyed with iron, it is used as an igniter for inflammable vapors in safety lamps. It dissolves in dilute acids, and slowly decomposes water.

79. Cerium and Oxygen.—Cerium forms three oxides, namely, the dioxide, CeO_2 , the sesquioxide, Ce_2O_3 , and the peroxide, CeO_3 . The first two are basic in character and form salts known as the *ceric* and *cerous*. The cerous salts are mostly colorless, while the ceric are yellow or brown.

80. Halogen Compounds of Cerium.—Thus far the only chloride of cerium that has been obtained is the cerous chloride having the formula $CeCl_3$. The *tetrafluoride*, CeF_4 , is obtained, however, by treating the hydroxide $Ce(OH)_4$ with hydrofluoric acid.

THORIUM

Symbol Th. Atomic weight 232.4. Valence IV.

81. Occurrence and Preparation.—Thorium was discovered by Berzelius, in 1828, in the mineral thorite found in Norway, which is essentially a silicate of thorium, having the formula $ThSiO_4$. By treating the tetrachloride with silicon or potassium, it is obtained free in the form of a dark-gray powder. When strongly heated in the air it ignites, burning with a bright flame, and forms *thorium dioxide*, ThO_2 . It has a specific gravity of 11.0, is difficultly soluble in hydrochloric acid, but is readily soluble in nitric acid and aqua regia. It is radio active.

82. Thorium and Oxygen.—Thorium dioxide, frequently called *thoria*, is formed when thorium burns in air. It is a pure white powder, almost entirely infusible, and is incandescent in high temperatures, giving a brilliant light. For this reason it is largely used, in connection with a few other rare oxides, for the manufacture of the mantles used in the Welsbach light.

Unlike the other members of the group, thorium dioxide does not form thorates, but acts as a base, forming salts in which thorium acts as a quadrivalent element.

83. Halogen Compounds of Thorium.—*Thorium tetrachloride, ThCl_4* , is obtained by heating an intimate mixture of the dioxide and carbon in dry chlorine. It is not decomposed by water at ordinary temperature, but if its solution in water is evaporated, hydrochloric acid is evolved and thorium dioxide remains. With potassium chloride, the tetrachloride forms potassium chlorthorate, K_2ThCl_6 .

Thorium tetrafluoride, ThF_4 , is obtained as a white powder by treating the tetrachloride with hydrofluoric acid. It unites with potassium fluoride, forming *potassium fluothorate, K_2ThF_6* .

INORGANIC CHEMISTRY

(PART 8)

FAMILY 1, GROUP A

INTRODUCTORY

1. The division of the elements into *metals* and *non-metals* was at first based on physical properties. The elements that possessed metallic luster, were opaque, and were good conductors of heat and electricity were known as **metals**; the elements that did not possess these properties, or possessed them in a much less marked degree, were classed as **non-metals**. Gradually, however, the chemical character of the element became the chief factor in deciding to which class it belonged, until at present the principal consideration in deciding whether an element shall be classed as a metal or non-metal is whether its oxides and hydroxides are acidic or basic. If the element is base forming, it is usually considered as a metal; if it is acid forming, it is classed as a non-metal. This division is not perfect, however, for some elements form both bases and acids. On this account, it is best to lay less stress on the classification as metals and non-metals, and base our classification on the natural division, known as the periodic system. Though this system has been followed in the preceding Sections, it will be noticed that the list of elements already treated very nearly coincides with the list of elements usually treated as non-metals, while those that remain to be treated are nearly identical with those usually classed as metals.

The metals usually occur in nature in the form of compounds called *ores*; their extraction from which has grown into a science known as *metallurgy*. It would be impossible to give a complete description of all the processes for the preparation of the metals in a work of this character, and consequently only those that best illustrate the chemical principles involved will be given.

The chemical activity of those elements already studied varies inversely with the atomic weight; that is, the element having the lowest atomic weight is the most active. For example, the oxides of nitrogen are strongly acidic, those of phosphorus and arsenic less so, while those of bismuth seem to be basic rather than acidic. The same thing is generally true of the metals. The lighter members of a group are the most active chemically, while the heavier ones are much less active. As a rule, the lighter metals form strong bases, while the heavier ones form weak bases, and in some cases act also as acid-forming elements.

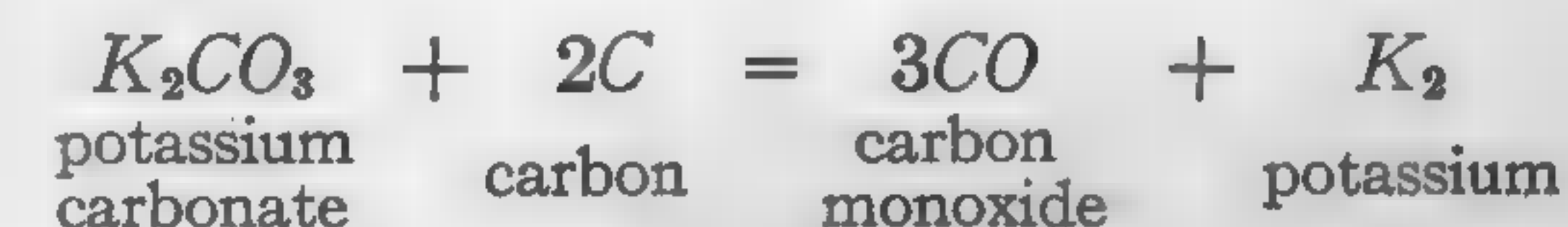
2. Family 1, Group A, generally called the *alkalies*, consists of the elements *lithium*, *sodium*, *potassium*, *rubidium*, and *cæsium*. They are all soft metals having a silvery luster, and are easily melted and volatilized. As their atomic weights become greater their melting and boiling points become lower, and their specific gravities become higher. Of all the metals they are the most strongly electropositive. Of these, sodium and potassium are most abundant, lithium is not nearly so common, and rubidium and cæsium are quite rare. The hydroxides of these metals are soluble in water, and are the strongest bases known; they unite with all acids, forming salts that are, as a rule, very stable. The members of this group act as univalent elements. As potassium and sodium are the most abundant and important members of this group, they will be treated first.

POTASSIUM

Symbol K. Atomic weight 39.1. Valence I.

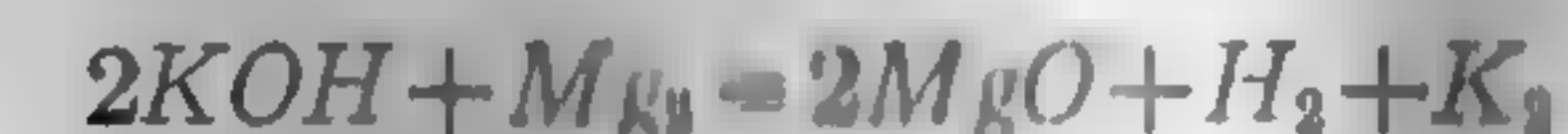
3. History and Occurrence.—The discovery of potassium dates back to 1807, when Sir Humphrey Davy, by submitting potassium hydrate to electrolysis, obtained this metal; soon after, Gay-Lussac and Thenard prepared it chemically in the pure state. Though rather abundant in nature, it is found only in combinations, and never pure. In the mineral kingdom it occurs as nitrate or saltpeter, as chloride or sylvite, as potassium-magnesium chloride or carnallite, and as sulphate or apthitalite. It is also found in various combinations in the waters of the ocean and mineral springs, as well as in land plants, and it appears to be essential to animal life.

4. Preparation and Properties.—At present potassium is prepared by decomposing potassium carbonate by carbon at high temperature, according to the equation:



The mixture is heated to whiteness in an iron retort, and the vapors are passed into a copper receiver. The potassium distils over and condenses in globules, still containing carbon in the form of charcoal. It is purified by redistillation in an iron retort, and is condensed in a copper receiver filled with naphtha.

The manufacture of potassium is rather dangerous, owing to the formation of a very explosive compound of potassium and carbon monoxide, which has the composition $C_6O_6K_6$. It has been lately proposed to manufacture this metal by heating potassium hydroxide, KOH , with magnesium, the potassium distilling off in the current of evolved hydrogen:



Potassium can be prepared also by the method for the manufacture of sodium by electrolysis, which will be described later.

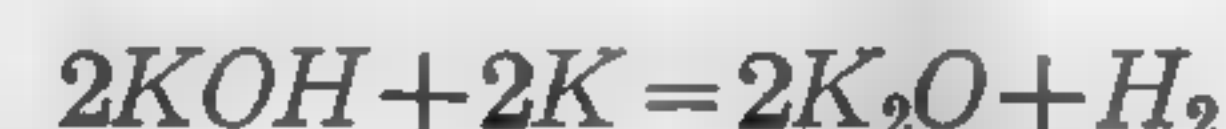
It can be prepared on a small scale by the electrolysis of fused potassium cyanide, or a fused mixture of potassium chloride and calcium chloride.

Potassium is a soft, brilliant, bluish-white metal, tarnishing instantly, however, in the air to a dull, grayish color. It must always be preserved under naphtha. It possesses a specific gravity of .875, becomes brittle at 0° C., and melts at 62.5° C. to a liquid closely resembling mercury; from this it may be crystallized in tetragonal octahedrons. It may be distilled in hydrogen and gives a green vapor.

Thrown on water, it at once decomposes it, evolving so much heat that the hydrogen, set free, takes fire and burns with a characteristic violet flame. It unites actively with chlorine and with sulphur. Its spectrum is characterized by two sharply defined lines—one in the red, having a wave length of .000768 millimeter, and the other in the violet, having a wave length of .0004045 millimeter. By means of this spectrum, as minute a quantity of potassium as $\frac{1}{3000}$ milligram may be detected with absolute certainty.

POTASSIUM OXIDES

5. *Potassium oxide*, K_2O , is obtained by the direct oxidation of the metal, as when it is burned in air or oxygen and the product is ignited, or when potassium hydroxide is heated with potassium, according to the equation:

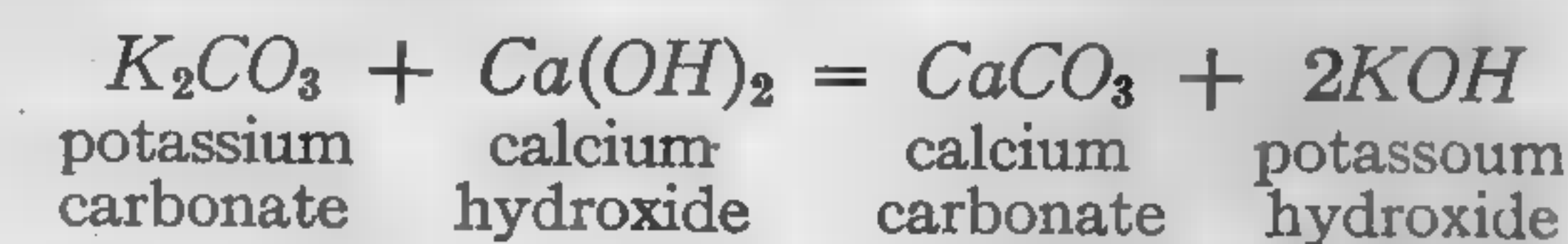


It is a grayish-white, deliquescent, caustic substance, and unites energetically with water to again form the hydroxide.

Potassium peroxide, K_2O_4 , is formed when potassium is burned in air or oxygen. At high temperatures it decomposes into potassium oxide, K_2O , and oxygen. It is a strong oxidizing agent, readily giving up oxygen to oxidizable substances.

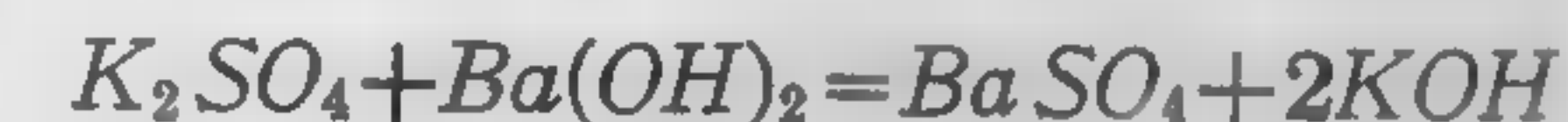
Potassium hydroxide, KOH , or potassium hydrate, commonly known as *caustic potash*, is prepared by boiling 1 part of potassium carbonate with 12 parts of water, and gradually adding milk of lime to the boiling liquid. The calcium com-

bines with the carbonic acid, forming an insoluble carbonate, while the potassium hydroxide remains in solution.



When the decomposition is finished, the liquid is allowed to settle, and the clear solution is decanted and rapidly evaporated. The residue is melted in a silver dish and poured out on flat stone slabs. This product is impure, and by treating it with alcohol, which dissolves only the potassium hydroxide, it may be freed of lime and any salts of potassium it may possess—especially of the carbonate, which is formed by the absorption of carbon dioxide from the air during evaporation. The clear alcohol solution is decanted, and after the alcohol has been expelled by distillation, the residue is evaporated to dryness and fused in a silver dish.

Potassium hydroxide, which is perfectly pure chemically, is frequently used in the laboratory, and may be prepared by double decomposition between potassium sulphate and barium hydroxide, the potassium-hydroxide solution being separated by decantation from the insoluble barium sulphate:



It is frequently prepared also by the electrolysis of solution of potassium chloride.

Recently fused potassium hydroxide occurs as opaque, white fragments having a short fibrous fracture. It melts just below a red heat to an oily liquid, and volatilizes at whiteness; it is not decomposed by heat. When exposed to the air, it absorbs moisture as well as carbon dioxide from the atmosphere, and deliquesces. It is very soluble in water. A hydrate having the composition $KOH \cdot 2H_2O$ is deposited from its hot and very concentrated solution, in rhombohedral crystals.

Potassium hydroxide is very caustic; it softens and partly destroys the skin, and is, for this reason, employed as a caustic in surgery. It shows the properties of an alkali in the highest degree; these are, its solubility in water, its power to neutralize the acids and to decompose a great number of metallic solutions,

and its corrosive action on the tissues. This alkalinity may be shown by the energy with which the most dilute solutions of potassium hydroxide restore the blue color to reddened litmus.

SULPHIDES OF POTASSIUM

6. Potassium sulphide, K_2S , is obtained by passing hydrogen over heated potassium sulphate, or by gently heating a mixture of potassium sulphate and carbon, thus:

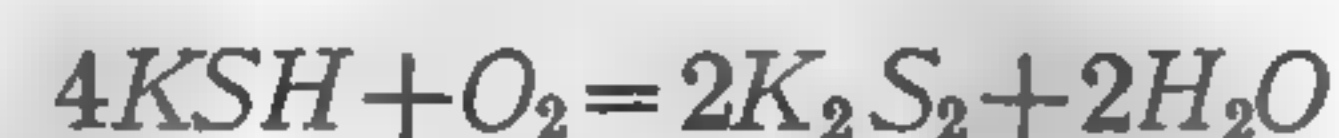


The sulphide obtained by using hydrogen is a red, crystalline mass, whereas a flesh-colored porous mass is obtained when carbon is used. A solution of the sulphide can be obtained by saturating a solution of potassium hydrate with hydrogen sulphide and adding an equal quantity of the hydrate. If the sulphide is fused it solidifies in a red, crystalline mass, which is deliquescent in moist air and is soluble in water.

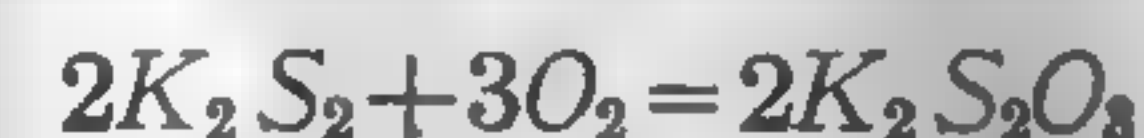
7. Potassium hydrosulphide, KSH , may be prepared by treating potassium carbonate heated to dull redness with hydrogen sulphide, as shown in the equation:



It forms a white or yellow deliquescent solid that is very soluble in water, melts at about $500^\circ C.$ to a yellow liquid, and at a higher temperature turns to a dark red. Exposed to the air its aqueous solution becomes yellow from the formation of the disulphide, thus:



If exposed for a longer time, the solution becomes colorless, potassium thiosulphate being formed, thus:



POTASSIUM AND CHLORINE

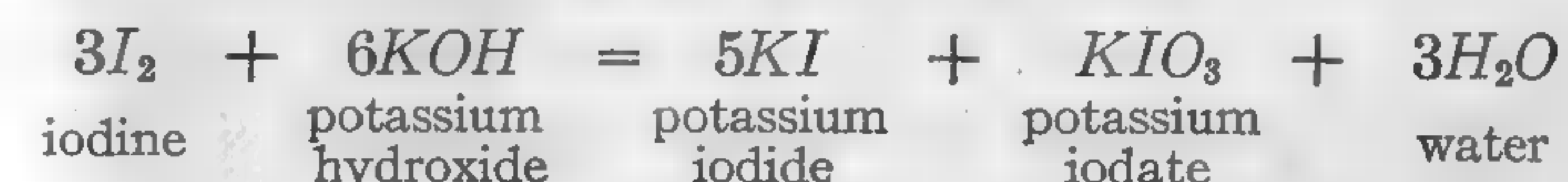
8. Potassium chloride, KCl , constitutes the mineral *sylvite*, and closely resembles rock salt. It is obtained commercially from sea-water, from kelp (the ash of seaweed), from the

refuse of the manufacture of sugar from beet root, or from an abundant mineral of the Stassfurt mines, *carnallite*, which is potassium-magnesium chloride. It is a transparent, colorless solid that crystallizes in cubes; it has a specific gravity of 1.98 and a bitter, salty taste. It is soluble in water and produces a depression of temperature in dissolving. One part of potassium chloride dissolves in 3 parts of water at $17.5^\circ C.$; 100 grams of water at $0^\circ C.$ dissolves 29.23 grams of potassium chloride and .2738 gram additional for each degree rise in temperature.

POTASSIUM AND IODINE

9. Potassium iodide and bromide are commercially important on account of their use in medicine and photography.

Potassium iodide, KI , is prepared on a large scale by the direct action of iodine on potassium hydroxide:



Potassium iodide and iodate are formed, the latter being precipitated. The whole is evaporated to dryness, and the residue heated to redness with powdered charcoal, whereby the iodate is converted into iodide. The mass is dissolved in hot water; on cooling, the solution deposits the iodide in fine, colorless, transparent cubes. One hundred parts of water at $18^\circ C.$ dissolves 143 parts of potassium iodide; it is also readily soluble in alcohol. A solution of potassium iodide dissolves iodine readily.

Potassium bromide, KBr , is similar in properties to the iodide and is obtained by an analogous process. It crystallizes in cubes that are soluble in about 1.5 parts of cold water.

SALT OF POTASSIUM

10. Potassium nitrate, KNO_3 , long known as saltpeter or niter, is found in some parts of India, in Egypt, Persia, Hungary, Spain, etc., where it sometimes appears as a white incrustation on the surface of the soil and is sometimes mixed

with the soil to some depth. The saltpeter is extracted from the earth by treating the earth with water; the solution formed is evaporated, at first by the heat of the sun and afterwards by artificial heat, when the impure crystals are obtained, which are exported as *grough* (or impure) saltpeter. It is far less abundant in northern climates than in southern. It is formed wherever nitrogenized organic substances decompose in the presence of potassium hydroxide, and is manufactured, artificially, by exposing to the air mixtures of animal matters with wood ashes and lime, moistened with stable drainings or stale urine. The greater part of the saltpeter of commerce is now obtained from sodium nitrate, of which enormous deposits occur in Peru and Chile.

The conversion of this so-called *Chile saltpeter* into potassium nitrate is effected in the following manner: The recrystallized sodium nitrate is dissolved in water, and an equivalent quantity of potassium chloride, which is abundantly obtained from the Stassfurt mines, is added, when a double decomposition takes place. The solution is boiled down; the hot liquid deposits sodium chloride, which is separated, and potassium nitrate crystallizes out on cooling.

Potassium nitrate crystallizes from its aqueous solution in long, six-sided prisms that have a cool and slightly bitter taste. It melts at 340°C .; at a higher temperature it disengages oxygen and is converted into *potassium nitrite*, KNO_2 , which in its turn is decomposed at a red heat, leaving a mixture of oxide and peroxide of potassium. Potassium nitrate is very soluble in water, the solvent power of the water increasing as its temperature rises. While 100 parts of water at 0°C . dissolves only 13.33, at 100°C . it dissolves 246 parts. Potassium nitrate is largely used in the manufacture of gunpowder, which is an intimate mixture of niter, charcoal, and sulphur.

11. Potassium sulphate, K_2SO_4 , is found in certain salt mines in the mineral *kainit*, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. It is also largely obtained as a secondary product in various manufacturing processes. It deposits from the mother liquors

of the soda from seaweed when these are exposed to low temperatures. It may be obtained by saturating, with potassium carbonate, the acid potassium sulphate that is formed in the preparation of nitric acid by the decomposition of potassium nitrate with sulphuric acid. It is prepared also by the action of concentrated sulphuric acid on potassium chloride. Potassium sulphate melts at 1050°C ., is soluble in about 10 parts of cold water, but in a much smaller quantity of boiling water; it has a bitter taste and is neutral to test paper. Its crystals are a combination of rhombic pyramids and prisms, resembling those of quartz in formation and appearance; they are anhydrous and decrepitate when suddenly heated, which is often the case with anhydrous crystals, that is, those that contain no water of crystallization. They are insoluble in alcohol.

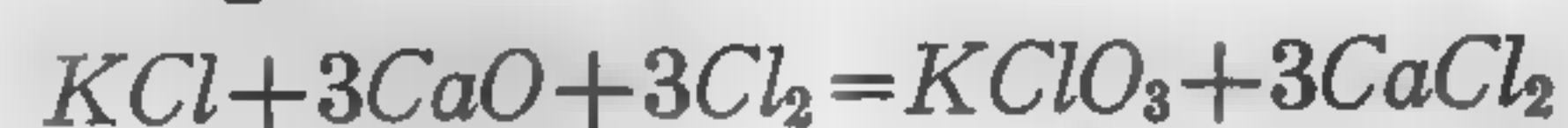
12. Acid potassium sulphate, KHSO_4 , commonly known as *potassium bisulphate*, may be prepared by mixing potassium sulphate with half its weight of concentrated sulphuric acid, and evaporating the mixture to dryness in a platinum vessel; the fused salt thus obtained is then dissolved in hot water and left to crystallize. The crystals are either rhombic octahedrons or tabular crystals belonging to the orthorhombic system, and melt at about 200°C ., losing water and being converted into the pyrosulphate, $\text{K}_2\text{S}_2\text{O}_7$. They are much more soluble than the normal salt, requiring only twice their weight of water, having a temperature of 15.5°C . and half that quantity at 100°C .; the solution is acid and has a sour taste.

13. Potassium chlorate, KClO_3 , is formed, together with potassium chloride, by the action of an excess of chlorine on a concentrated solution of potassium hydrate or carbonate, thus:



In the arts, potassium chlorate is obtained by the action of chlorine on a mixture of lime, potassium chloride, and water heated in closed vessels. Chlorate and chloride of calcium are formed, and in the presence of the potassium chloride a double decomposition takes place, potassium chlorate and

calcium chloride, which latter is very soluble, being formed. The liquid is filtered hot, and the potassium chlorate crystallizes out on cooling:



These methods are now being replaced by the electrolytic method. A solution of potassium chloride is electrolyzed when caustic potash and chlorine are formed. These react upon each other and by allowing the reaction to continue, the solution is finally converted into potassium chlorate.

Potassium chlorate melts at 334° C., and at a higher temperature is decomposed into oxygen, potassium perchlorate, and potassium chloride. Potassium chlorate deflagrates when thrown upon hot coals; when mixed with sulphur, it explodes by friction or percussion. It is a powerful oxidizing agent, is soluble in about 20 parts of cold and 2 parts of boiling water; the crystals are anhydrous, flat, and tabular, and in taste somewhat resemble potassium nitrate.

14. Potassium perchlorate, $KClO_4$, is formed by the action of either heat or sulphuric acid on potassium chlorate. It is remarkable for its sparing solubility, for it requires 70 parts of cold water to dissolve it. It crystallizes in anhydrous, transparent, right rhombic prisms, and above 400° C. decomposes into potassium chloride and oxygen.

15. Potassium carbonate, K_2CO_3 , is met in commerce in the impure condition, under the name *potash*. It is obtained by lixiviating wood ashes; that is, exhausting them with water, evaporating the solution to dryness, and calcining the residue in the air. The potash thus obtained is impure potassium carbonate, mixed with various other salts of potassium, such as the chloride and sulphate and silicate, and only contains, approximately, from 60 to 80 per cent. of carbonate. Potassium carbonate is now manufactured on a large scale from the native chloride, so-called *Stassfurt salt*, by a similar process to that described for the manufacture of sodium carbonate from common salt.

Potassium carbonate is found also in the wool of sheep. The liquors obtained from the washing of the wool are evaporated

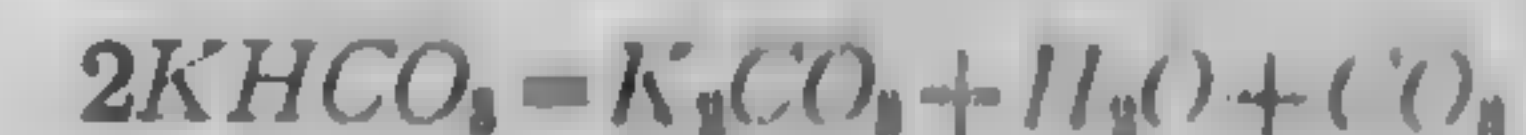
to dryness, and the residue burnt in retorts. The refuse yeast rising during the fermentation of wines is used as a source of potassium carbonate. The yeast is dried and then burned in a retort.

16. Pure potassium carbonate forms a white granular powder or a white solid mass very soluble in water; it has a strong alkaline reaction, and a slightly caustic taste. It is insoluble in alcohol. It melts at 880° C., and volatilizes at a white heat. It absorbs moisture readily from the air. Potassium carbonate is largely employed for various purposes in the arts, and is a compound of considerable importance.

17. Acid potassium carbonate, $KHCO_3$, or *potassium bicarbonate*, being much less soluble than the normal salt, crystallizes out of solution when a concentrated solution of the normal salt is treated with carbon dioxide, thus:



It is prepared also by passing carbon dioxide over moist potassium carbonate and recrystallizing the product from warm water. It crystallizes in large transparent monoclinic prisms, without water of crystallization. It has a salty taste and an alkaline reaction. Heated to 190° C., or by boiling the aqueous solution, carbon dioxide is evolved and water is given off with the formation of the normal salt according to the equation:



18. Potassium Phosphates.—*Potassium orthophosphate, K_3PO_4 ,* formed by igniting phosphoric acid with excess of potassium carbonate, is readily soluble in water and crystallizes in small needles. The secondary salt, K_2HPO_4 , obtained by mixing aqueous phosphoric acid with a quantity of carbonate of potassium sufficient to produce a slight alkaline reaction, and evaporating, is easily soluble in water, but does not crystallize. The primary salt, KH_2PO_4 , obtained by using a slight excess of phosphoric acid, forms small needle-shaped crystals, which are easily soluble in water, but insoluble in alcohol. It is used in artificial fertilizers.

Potassium pyrophosphate, $K_4P_2O_7$, is deliquescent and separates from aqueous solution in fibrous crystals. It is formed by the heating of the secondary orthophosphate. The acid salt, $K_2H_2P_2O_7$, separates as a deliquescent mass on adding alcohol to a solution of the normal pyrophosphate in acetic acid.

Potassium metaphosphate, KPO_3 , is almost insoluble in water; the dimetaphosphate, $K_2P_2O_6 \cdot H_2O$, prepared by decomposing the corresponding copper salt with potassium sulphide, is soluble in water and crystallizable; it is converted by ignition into the monometaphosphate.

19. Potassium Arsenates.—The *neutral salt*, K_3AsO_4 , is obtained by treating arsenic acid with an excess of potassium carbonate. The secondary salt, K_2HAsO_4 , is crystallized with difficulty. The primary salt, KH_2AsO_4 , forms large crystals.

20. Potassium Arsenites.—The salt $KH_3As_2O_6$ is obtained as a crystalline powder on adding alcohol to a solution of arsenious oxide in the minimum quantity of potassium carbonate. When heated with a solution of potassium carbonate, it is converted into the meta-arsenite, $KAsO_2$, which in turn, when heated with potassium hydroxide, yields the *diarsenite*, $K_4As_2O_6$.

A solution of potassium arsenite, known in medicine as *Fowler's solution*, is prepared by boiling 1 part of arsenious oxide with 1 part of potassium carbonate in distilled water, and diluting to 90 parts of solution.

21. Potassium Borates.—The *metaborate*, KBO_2 , is obtained by fusing a mixture of boric acid and potassium carbonate; it is only slightly soluble in water and separates in small monoclinic crystals. It has an alkaline reaction and absorbs carbon dioxide from the air, being thereby converted into the *pyroborate* or *tetraborate*, $K_2B_4O_7$. This latter, which is also formed on mixing a solution of boric acid with a slight excess of potassium carbonate, is easily soluble, and crystallizes in hexagonal prisms containing $5H_2O$.

The *triborate*, $2KB_3O_5 \cdot 5H_2O$, is formed on mixing the hot solution of boric acid and potassium carbonate, and separates in glittering rhombic crystals.

The *pentaborate*, $2KB_5O_8 \cdot 4H_2O$, separates in rhombic octahedrons from a hot solution of potassium hydroxide saturated with boric acid.

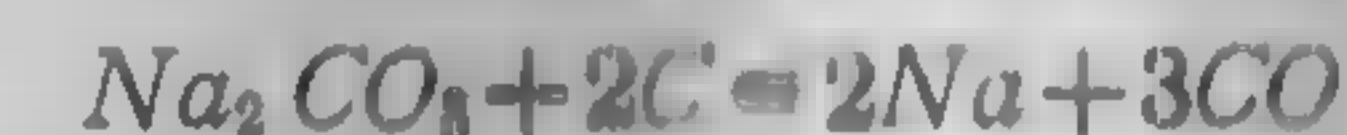
22. Potassium Silicates.—A silicate of potassium is formed when silica is fused with potassium carbonate. Its composition appears to vary. It is soluble in water, and on evaporating in air the solution deposits a glassy-appearing substance. For this reason it is called *water glass*. It may be prepared also by dissolving silicon dioxide in potassium hydroxide.

SODIUM

Symbol Na. Atomic weight 23. Valence I.

23. History and Occurrence.—Though sodium oxide was already recognized in the year 1736 by Duhamel, the metal in the pure state was only obtained in 1807 by Sir Humphry Davy. Sodium does not occur in the free state in nature, but is found abundantly in combinations. Its chloride, or salt, is known as the mineral *halite*, and is found not only in immense deposits of rock salt but also in enormous quantities in sea-water and in the waters of saline springs. Sodium also occurs in the form of nitrate, or Chile saltpeter; of borate, or borax; of carbonate, or trona; and of silicate, in albite, oligoclase, sodalite, etc. It is found in marine plants, and is essential to animal life.

24. Preparation and Properties.—Sodium until recently was prepared by distilling a mixture of sodium carbonate and carbon, when the metal distils over, according to the equation:



It was prepared also by reducing its oxide by carbon at a white heat, thus:



Practically, 30 kilograms of dry sodium carbonate, 13 kilograms of charcoal, and 3 kilograms of calcium carbonate were intimately mixed together, calcined, and introduced into iron

cylinders heated in a reverberatory furnace. At a bright-red heat the sodium distilled over, and was collected in receivers. To purify it, it was redistilled, melted under petroleum, and cast into ingots, which must be preserved under naphtha.

These processes have been almost entirely superseded by electrolytic methods—the electrolysis of the hydroxide. In this method fused sodium hydroxide is electrolyzed in an iron vessel. The metallic sodium, being lighter than the hydroxide, rises, together with the hydrogen, from the negative pole and is collected in a receiver. The hydrogen escapes around the edges of the cover of the receiver. More sodium hydroxide is added from time to time to replace the metal removed, thus making the process continuous.

Sodium is a lustrous, silver-white, soft metal; its specific gravity is .972; it becomes brittle at -20°C ., melts at 95.6°C ., and boils at 742°C . It crystallizes in tetragonal octahedrons. On exposure to air it rapidly tarnishes, and if thrown on water, decomposes it with effervescence; if it is prevented from moving, or if the water is warm, it takes fire, burning with a characteristic yellow flame, and yields a spectrum consisting of a double yellow line with a wave length of .0005892 millimeter. Sodium is far less costly than potassium, and is used on a large scale for the extraction of the metal magnesium and for making sodium peroxide. An amalgam of sodium is also employed with advantage in extracting gold and silver from their ores.

COMPOUNDS OF SODIUM

25. Sodium chloride, NaCl , is common salt, or sea salt. It is widely diffused in nature and is found in the solid state, as rock salt, in many countries. Sea-water contains a large proportion of sodium chloride, and it exists also in various mineral springs. It may be formed by the direct union of its constituents, as by burning sodium in chlorine gas. It is obtained commercially either by mining it directly, in which form it is known as rock salt, or by evaporating either sea-water or the waters of saline springs, producing solar salt if the heat is natural, and boiled salt if artificial heat is employed.

Much of the salt of commerce was formerly obtained by the evaporation of sea-water along the Mediterranean. The water is let into basins a few inches deep, which are continually swept by the summer winds. It thus becomes concentrated, and is kept in motion from one basin to another, until it arrives in the areas where the salt is deposited.

Extensive beds of rock salt occur in Russia, France, Germany, Hungary, Spain, Abyssinia, Mexico, and various parts of the United States. Perfectly pure specimens of rock salt form beautiful, colorless cubes, and are known as *sal gemme*, but ordinary rock salt is only partly transparent and exhibits a rusty color, owing to the presence of iron. At Droitwich, Worcestershire, England, the salt is obtained by evaporation from the waters of certain saline springs. In some parts of France and Germany, where the water from the salt springs contains so little salt that it would not pay for the fuel necessary to evaporate the water, a very ingenious plan is adopted by which the proportion of water is greatly reduced without the application of artificial heat. The water is pumped to the top of a framework filled with bundles of twigs and brushwood, as shown in Fig. 1. The water, in trickling over the twigs and brushwood, exposes a large surface to the action of the wind and the sun, and a considerable evaporation takes place, so that a much stronger brine is collected in the reservoir beneath the scaffolding; by several repetitions of the operation the proportion of water is so far diminished that the rest may be economically evaporated by artificial heat.

26. Sodium chloride is a colorless, transparent solid that crystallizes from its aqueous solution in cubes. The crystals are generally very small, are anhydrous, and nearly equally soluble in hot and cold water. According to Gay-Lussac:

- 1 part of common salt dissolves in 2.78 parts of water at 14°C .
- 1 part of common salt dissolves in 2.70 parts of water at 60°C .
- 1 part of common salt dissolves in 2.48 parts of water at 109.7°C .

The saturated solution boils at 100.7°C .

The great tendency of ordinary table salt to become damp when exposed to the air is due chiefly to the presence of small



FIG. 1

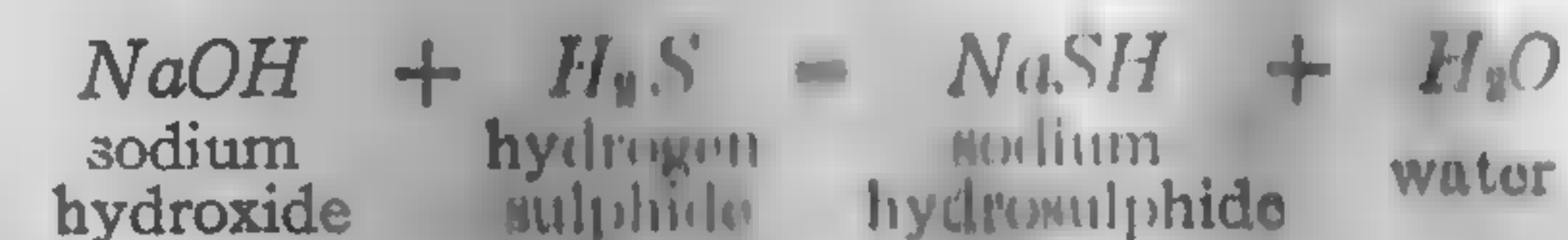
quantities of chlorides of magnesium and calcium, for pure sodium chloride has very little tendency to attract atmospheric moisture, although it is so easily dissolved by water.

27. Sodium Oxides and Sodium Hydroxide.—*Sodium oxide*, Na_2O , may be obtained by the combustion of sodium in air and heating the product with sodium; it is a white, fusible substance, uniting directly with water to form *sodium hydroxide*, NaOH . Sodium hydroxide, generally known as *caustic soda*, is frequently employed in the laboratory and in the arts. It is prepared, in the pure state, by the action of the metal on water; commercially, it is obtained by the action of calcium hydroxide—milk of lime—on sodium carbonate. The clear liquid thus obtained is evaporated in iron vessels, and the fused mass that is left is poured on to flat plates or cast in sticks. It is prepared also by the electrolysis of sodium chloride. It is a white, opaque, brittle solid of specific gravity 2.1. It is deliquescent and absorbs carbon dioxide from the air. It is freely soluble in water and may be obtained crystallized in prisms having the composition $2\text{NaOH} \cdot 7\text{H}_2\text{O}$.

Sodium peroxide, Na_2O_2 , is produced on a commercial scale by heating sodium to 300°C . in a current of dry air. It is a yellowish substance, turning white on exposure to air, and acts as a powerful oxidizing agent. Water decomposes it, forming sodium hydroxide and liberating oxygen. It is largely applied in bleaching silk and wool.

28. Sodium Sulphide and Hydrosulphide.—*Sodium sulphide*, Na_2S , may be obtained by reducing sodium sulphate. This may be accomplished by heating a mixture of sodium sulphate and carbon, or by heating the sulphate in a current of hydrogen.

Sodium hydrosulphide is prepared by the action of hydrogen sulphide on a solution of sodium hydroxide, according to the equation:



29. Sodium sulphate, Na_2SO_4 , or salt cake, is obtained abundantly, commercially, as a residue in various chemical processes, as, for instance, in the preparation of nitric and hydrochloric acid. It is also largely produced as an intermediate product in the manufacture of soda. It occurs in nature, anhydrous as *thenardite*, and hydrated as *mirabilite*. It crystallizes from solution in large, colorless prisms that have the composition $Na_2SO_4 \cdot 10H_2O$ and are efflorescent in dry air, losing all their water. This is Glauber's salt. The anhydrous salt is soluble in $2\frac{1}{2}$ parts of water at $100^\circ C$.

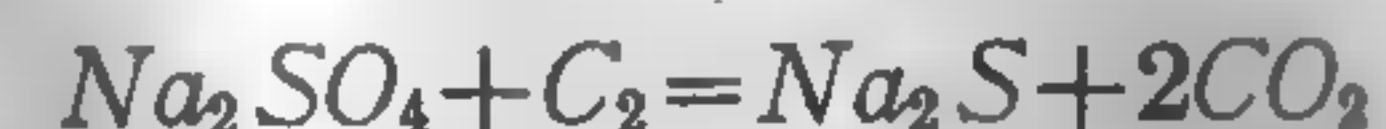
30. Acid sodium sulphate, $NaHSO_4$, is obtained by adding sulphuric acid to the neutral sulphate. On cooling the saturated solution, oblique rhombic prisms are obtained, which contain 2 molecules of water of crystallization. These crystals are very readily soluble in water, and have an acid taste. Alcohol decomposes them into sulphuric acid and neutral sulphate, which latter is precipitated.

31. Sodium carbonate, Na_2CO_3 , one of the most widely used salts, generally known as *soda*, or *soda ash*, is obtained on a very large scale by a number of methods. One of the oldest methods is that of Le Blanc. Previous to the year 1793 the larger portion of soda ash made was obtained from the ashes of the sea plant *salsola*.

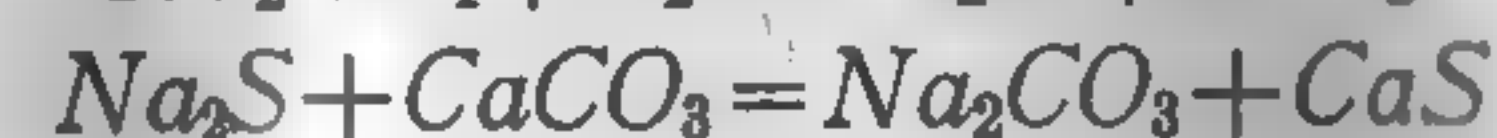
32. In the Le Blanc process salt and sulphuric acid are heated together, when the change shown in the following equation takes place:



The sodium sulphate, or *salt cake*, thus obtained is mixed with coal and limestone and again heated, when the sodium sulphate is converted into the carbonate in two steps represented by the equations:



and



The mixture of sodium carbonate and calcium sulphide, known as *black ash*, is leached with water, dissolving the soluble sodium carbonate from the insoluble calcium sulphide. The

solution is then evaporated, when the sodium carbonate crystallizes.

In this process the salt and sulphuric acid are charged into the pan *A*, Fig. 2, and are heated by the fire in the grate *C*. Large quantities of hydrochloric acid gas are evolved and these pass through the flue *B* to a brick tower, where they are condensed. The partly decomposed salt is then transferred to the muffle part *D* of the furnace, where the decomposition is completed. The hydrochloric acid gas evolved here passes to the condensing towers through the flue *E*.

For about each ton of soda ash produced there is about $1\frac{1}{2}$ tons of waste. This is recovered by pumping the carbon dioxide evolved in the burning of lime in tall closed cylinders

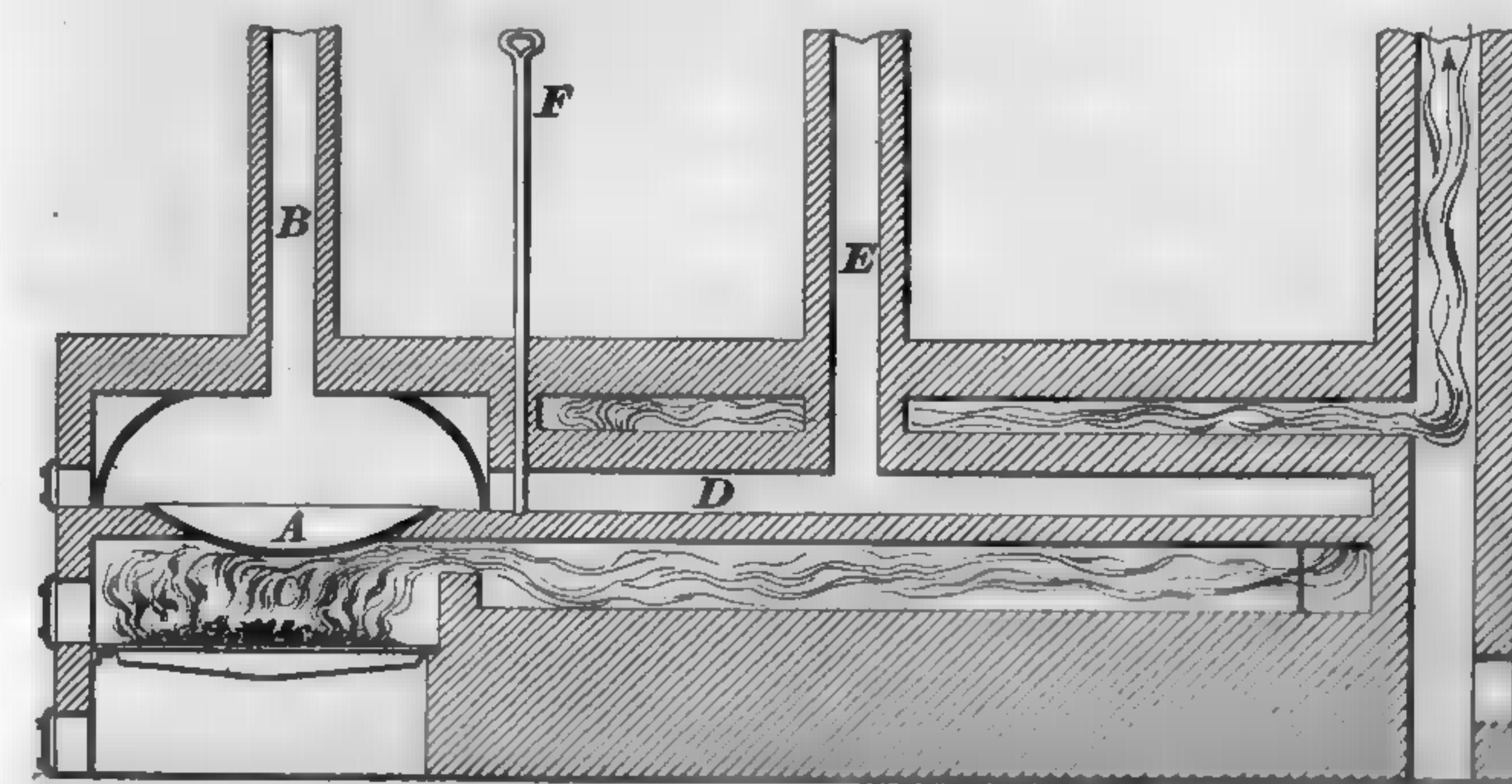
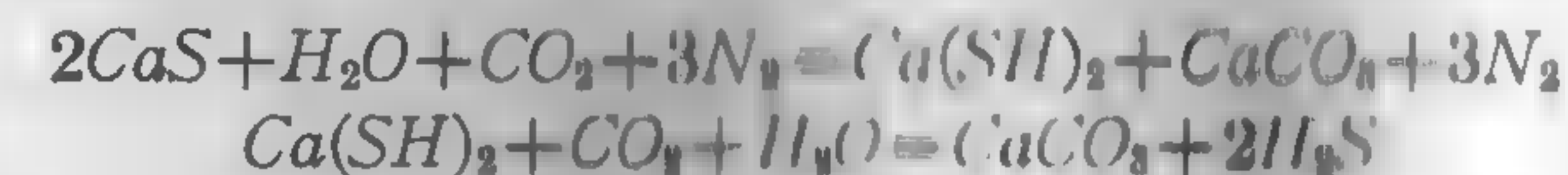


FIG. 2

containing the waste, which is mixed to a creamy consistency with water. The carbon dioxide first forms calcium hydrosulphide, calcium carbonate, and nitrogen. The calcium hydrosulphide is then converted into the carbonate with an evolution of hydrogen sulphide. These two steps are represented by the equations:

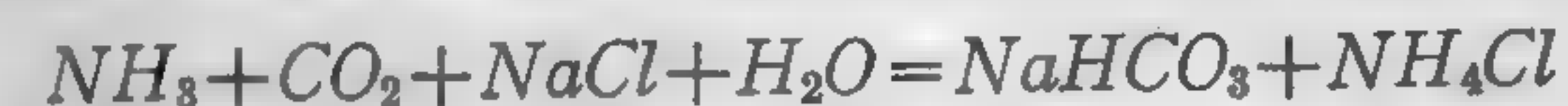


The hydrogen sulphide is then burned and produces sulphur and water.

33. The Solvay process, or the *ammonia-soda process*, has to a large extent superseded the Le Blanc process. This

process depends on the double decomposition that occurs when carbon dioxide is passed into a solution of sodium chloride containing ammonia. This process yields a purer product than the Le Blanc process, is less expensive, and gives rise to no noxious by products.

Brine obtained either directly from the mines or by dissolving rock salt is purified by treatment with calcium hydroxide, which removes the magnesium salt. The calcium salts are then removed by either sodium carbonate or weak solutions of ammonium carbonate, after which the brine is saturated with ammonia. The ammoniacal brine is forced into tall towers and carbon dioxide is forced in at the bottom of the towers. The reaction that takes place is represented by the equation:



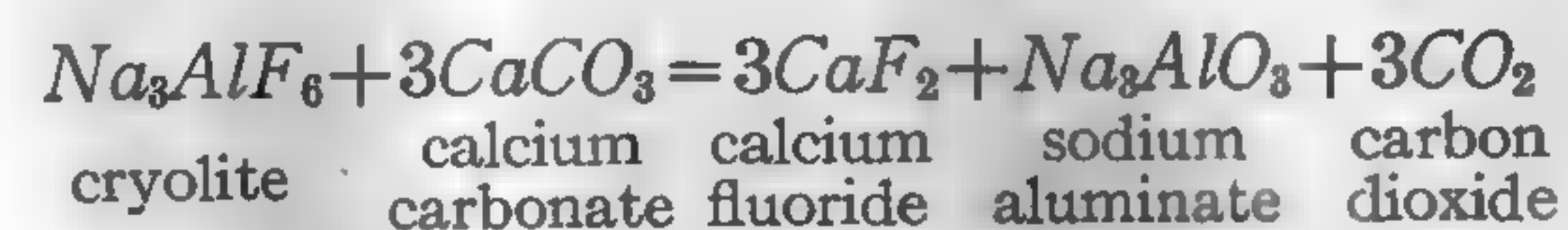
The sodium bicarbonate, in the form of a pasty liquid, is drawn off, washed, dried, and calcined, thus driving off the ammonium salts and converting the bicarbonate into the neutral carbonate, thus:



The carbon dioxide driven off is again utilized by being absorbed by fresh brine.

34. A considerable quantity of sodium carbonate is also produced from cryolite, of which large deposits exist in Greenland.

This mineral is calcined with limestone, calcium fluoride and sodium aluminate being formed, according to the equation:



The latter compound is dissolved by water and decomposed by carbon dioxide, aluminum hydroxide being precipitated and sodium carbonate remaining in solution.

35. The most satisfactory and successful electrolytic process is the **Castner-Kellner process**. In this process there is used a cell divided into three compartments. The center

compartment contains an iron cathode *a*, Fig. 3, that serves to decompose the sodium amalgam formed. The two end compartments serve as anode compartments and contain the carbon anodes *b*. One edge of the cell rests on a knife edge *c* and the other end is supported on the eccentric *d*, which revolves and thus slowly raises and lowers the end of the cell. Brine is placed in the two end compartments and is renewed, when necessary, by fresh brine flowing in; the exhausted brine goes to be resaturated. A thin layer of mercury covers the bottom of the apparatus, and is so regulated in amount that all of it

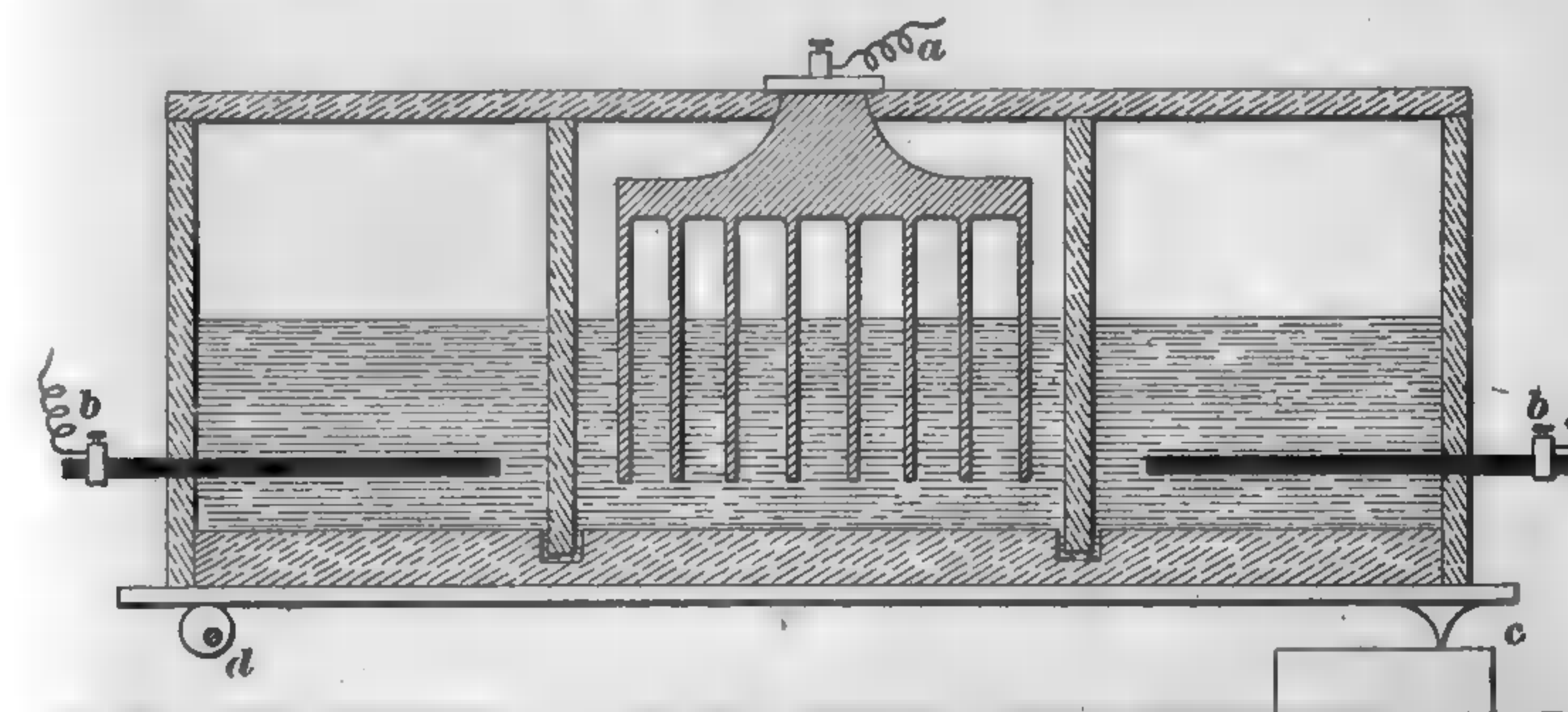


FIG. 3

practically flows alternately from the end compartments into the middle, as the cell rocks.

The salt is decomposed in the end divisions, the chlorine separating on the carbon anode and passing off, the sodium dissolving in the mercury cathode, forming sodium amalgam. As the cell tips the amalgam flows into the center compartment, where it forms the anode of a primary battery, and the iron electrode here becomes the cathode of this battery. Here the sodium and mercury are separated, the sodium going into solution as sodium hydrate, which is drawn off and converted into the carbonate.

36. Sodium carbonate crystallizes, at ordinary temperatures, with 10 molecules of water of crystallization in large monoclinic prisms that effloresce in the air and crumble to a white powder. It has an alkaline taste, and melts at 50° C.

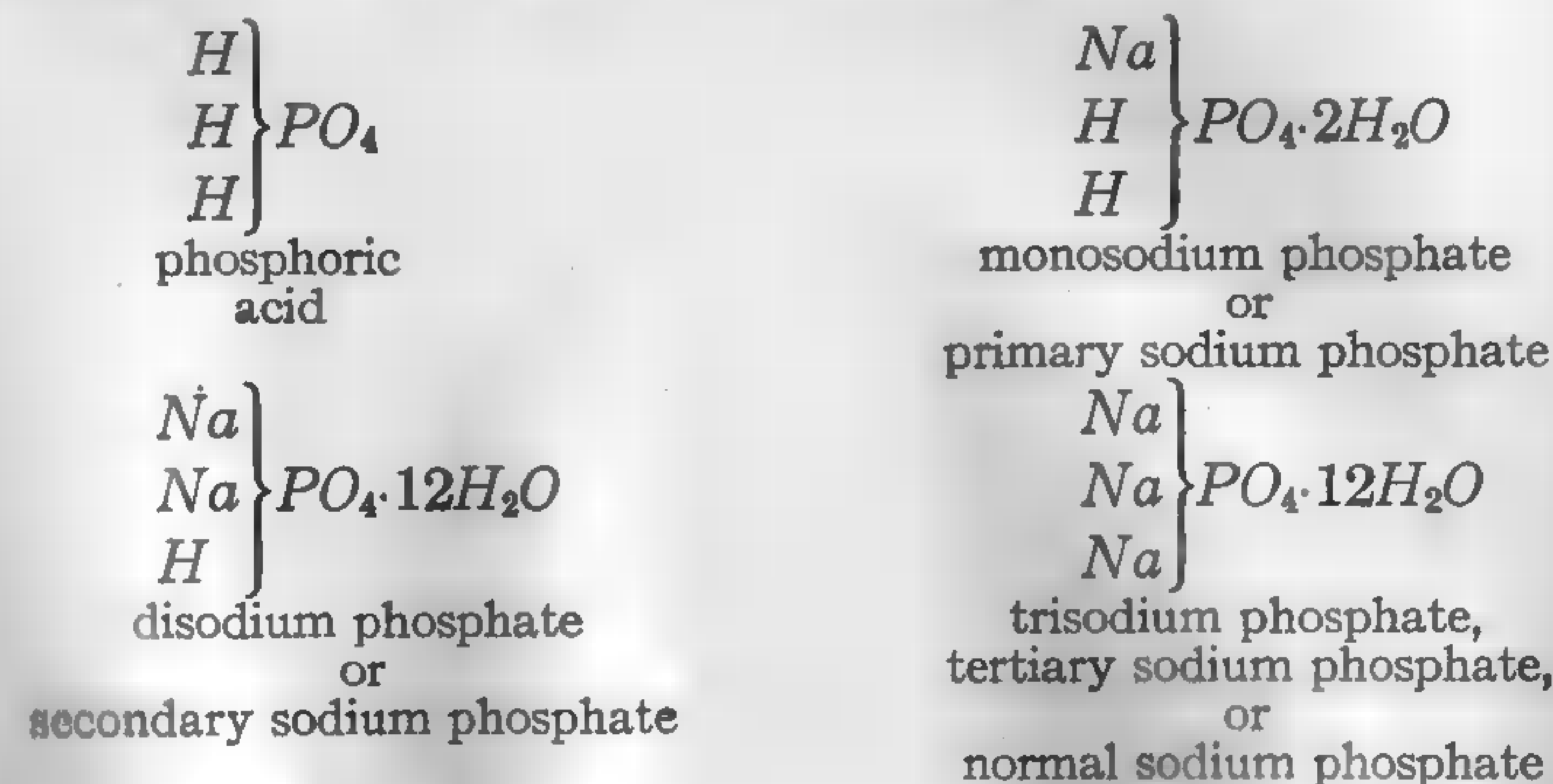
in its water of crystallization. It is soluble in water, the solution having a strong alkaline reaction. The solubility of sodium carbonate is well illustrated by the subjoined data:

100 parts of water at 0° C. dissolves 7.08 parts of sodium carbonate.
 100 parts of water at 10° C. dissolves 12.06 parts of sodium carbonate.
 100 parts of water at 20° C. dissolves 21.71 parts of sodium carbonate.
 100 parts of water at 25° C. dissolves 28.50 parts of sodium carbonate.
 100 parts of water at 30° C. dissolves 37.24 parts of sodium carbonate.
 100 parts of water at 104.6° C. dissolves 45.47 parts of sodium carbonate.

The saturated solution boils at 104.6° C. Sodium carbonate is insoluble in alcohol.

37. Acid sodium carbonate, sodium bicarbonate, or bicarbonate of soda, NaHCO_3 , is prepared by the action of carbon dioxide on the normal carbonate. It forms small monoclinic tabular crystals, or a white crystalline powder. It is less soluble in water than the normal carbonate, and the solution is much less alkaline. When boiled, its solution evolves carbon dioxide. The salt itself readily decomposes, when gently heated, into sodium carbonate, carbon dioxide, and water.

38. Phosphates of Sodium.—Three phosphates of sodium are obtained from phosphoric acid:



Monosodium phosphate, NaH_2PO_4 , is formed when phosphoric acid is added to a solution of sodium phosphate. It crystallizes with one molecule of water of crystallization; it has an acid reaction, and is soluble in water. At 100° C. it loses its water

of crystallization, and at 204° C. it loses a molecule of water and becomes *sodium metaphosphate, NaPO_3 .*

Disodium phosphate, Na_2HPO_4 , is the most stable and most important of the sodium phosphates. It is prepared by saturating phosphoric acid to a feebly alkaline reaction with sodium hydrate. It is best prepared commercially by treating bone ash with sulphuric acid and precipitating the calcium by means of sodium carbonate as dicalcium phosphate. Disodium phosphate crystallizes in large, transparent, monoclinic prisms with 12 molecules of water; they effloresce in the air, are soluble in water, giving an alkaline reaction, and melt at 35° C.

Normal sodium phosphate, Na_3PO_4 , or normal sodium orthophosphate, is made by adding 3 volumes of sodium hydrate to 1 volume of phosphoric acid. It crystallizes in six-sided prisms containing 12 molecules of water; these are soluble in water, have a strong alkaline reaction, and absorb carbon dioxide from the air.

39. Sodium Borate.—*Sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$,* better known as *borax*, occurs as a deposit from evaporation of the waters of certain lakes in Thibet and in the United States. It is also derived from the native borates of calcium and magnesium, such as *colemanite*, *borocalcite*, and *boracite*, which yield borax by a double decomposition with sodium carbonate.

When a concentrated boiling solution of borax is allowed to cool to 60° to 70° C. it deposits octahedral crystals containing 5 molecules of water, while below 60° C. it crystallizes in monoclinic prisms containing 10 molecules of water. This latter is the familiar form of commerce. It is somewhat soluble in water, its solution is faintly alkaline, and the crystals effloresce in the air, becoming opaque.

Borax glass is obtained by fusing the crystalline borax, which swells to a white spongy mass of many times its original volume; this mass afterwards fuses to a clear, glassy mass. It dissolves many metallic oxides very easily, and these impart their own peculiar color to the glass. It finds wide employment in blow-pipe analysis and in the metallurgical arts. It is antiseptic and is sometimes used as a preservative.

40. Sodium nitrate, NaNO_3 , or Chile saltpeter, is found in large quantities in Peru and Chile. It crystallizes in large rhombohedra very similar to cubes; hence, it is frequently called cubic niter, to distinguish it from the prismatic potassium niter. It is used as a fertilizer, and for the manufacture of nitric acid and potassium nitrate.

AMMONIUM

Formula NH_4 . Molecular weight 18.04. Valence I.

41. History.—The salts that ammonia forms by direct union show a great similarity to those formed by the metals potassium and sodium. To account for this remarkable similarity, Berzelius, in 1816, basing his ideas on a theory of Ampère, proposed to consider these salts as compounds of ammonium, NH_4 , a compound radical, capable of acting like the monad metals sodium and potassium. Being an unsaturated compound, ammonium, if it exists free, must have the formula $\text{H}_4 \text{N} \text{---} \text{N} \text{H}_4$, or, in other words, must exist as a double molecule with the formula N_2H_8 . Weyl, by condensing ammonia gas in the presence of sodium, obtained a bright-blue, metallic-like liquid, which he assumed to be *sodammonium* and to which he ascribed the formula $\text{N}_2\text{H}_8\text{Na}_2$. By acting on ammonium chloride with it, a similar blue liquid was obtained, which he considered to be free ammonium. Moreover, when mercury containing 1 per cent. of sodium is placed in a saturated solution of ammonium chloride, it increases considerably in bulk, becoming a pasty mass, which is the so-called *ammonium amalgam*.

42. Ammonium nitrate, NH_4NO_3 , is prepared by neutralizing nitric acid with ammonia. It crystallizes in large, transparent prisms melting at 166°C ., it is very soluble in water, alcohol, and liquid ammonia, and produces a notable depression of temperature in the act of solution. Heated gently, it decomposes into nitrous oxide and water. It is used largely for the manufacture of nitrous oxide (*laughing gas*), for the preparation of freezing mixtures, and for explosives.

43. Ammonium nitrite, NH_4NO_2 , forms colorless deliquescent crystals. Its solution decomposes, on heating, into nitrogen and water, as does the salt itself. A mixture of ammonium chloride and potassium nitrite is used for preparing nitrogen.

44. Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, is obtained when ammonia gas is passed through a solution of commercial ammonium carbonate. Exposed to the air, it gives off ammonia and becomes the bicarbonate. It is usually prepared by distilling a mixture of 2 parts of chalk and 1 part of ammonium sulphate in an iron retort connected with a leaden receiver. The fibrous product obtained is then resublimed in iron vessels having a lead dome. The ammonium carbonate obtained consists really of a mixture of the bicarbonate and ammonium carbonate. This is treated with strong alcohol, the carbonate being dissolved and the bicarbonate being left.

45. Ammonium bicarbonate, $(\text{NH}_4)\text{HCO}_3$, is formed when ammonium hydroxide is saturated with carbon dioxide. It forms a white, odorless powder, slightly soluble in water, and having a salty taste. Its aqueous solution slowly decomposes into the normal carbonate with the evolution of carbon dioxide.

46. Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, is obtained in the arts by passing the ammonia, which is disengaged when gas liquor is heated with lime, into dilute sulphuric acid. It crystallizes in right rhombic prisms, is colorless, and has a sharp taste. It dissolves in 2 parts of cold water and in its own weight of boiling water. It is insoluble in alcohol. It is manufactured on an extensive scale, and is used as a fertilizer and for the manufacture of other ammonium salts.

47. Ammonium chloride, NH_4Cl , was formerly obtained from Egypt, where it was made by subliming the soot produced by the combustion of camel's dung. It is now produced on a large scale from gas liquor, or the water condensed in the manufacture of illuminating gas from coal. This liquor is heated with lime; ammonia is disengaged and is conducted into hydro-

chloric acid. Ammonium chloride is obtained by simply evaporating the solution. It is then purified by sublimation in stoneware pots, which are heated in a furnace, out of which the upper parts of the pots project. The volatilized chloride condenses, and the sublimed product is known in trade as *sal ammoniac*, or *muriate of ammonia*.

It generally occurs as a white or grayish compact mass (having a crystalline fibrous structure), which is often striped with brown, owing to the presence of a little iron. It has a sharp and salty taste and dissolves in $2\frac{1}{2}$ parts of cold water, and in its own weight of boiling water. It is deposited from a saturated solution in small octahedral crystals, grouped together in needles, which thus present a fern-leaf appearance. At a high temperature it volatilizes without melting.

48. Ammonium sulphide, $(\text{NH}_4)_2\text{S}$, in the form of a white crystalline mass is obtained by mixing 1 part of hydrogen sulphide gas with 2 parts of ammonia gas in a vessel cooled by a mixture of salt and ice. It is readily soluble in water, and is rather unstable, decomposing at ordinary temperature into free ammonia and ammonium hydrosulphide, NH_4HS .

When strong ammonium hydrate is saturated with hydrogen sulphide at a low temperature, a colorless solution of NH_4HS results. In contact with the air this soon becomes yellow from the formation of *ammonium polysulphides* $(\text{NH}_4)_2\text{S}_x$. This latter solution is obtained more readily by adding sulphur to the ammonium hydrate previous to the saturation with hydrogen sulphide.

49. Ammonium bromide, NH_4Br , and **ammonium iodide**, NH_4I , are largely employed in photography. The former crystallizes in white cubes having a pungent, salty taste; it is volatile at a high temperature without decomposition, and is soluble in water and alcohol. The latter crystallizes in colorless cubes, which gradually become yellow and even brown from the separation of iodine. It is hygroscopic and odorless, has a sharp, saline taste and is extremely soluble in water and alcohol. It is volatile at a high temperature with decomposition without melting.

50. Ammonium chloride, NH_4Cl , or *sal ammoniac* is found in fissures and cracks of volcanoes and in recent lava streams. It has been noticed also where large masses of coal have burned, and is found in guano. At present it is prepared from the ammonia liquors of gasworks; this crude product is purified by recrystallization or by sublimation.

The pure salt is colorless and odorless, has a sharp, salty taste, and crystallizes from its aqueous solution in small feather-like octahedra or cubes. It is only slightly soluble in water, and reduces the temperature in the act of solution. It sublimes without melting, suffering a partial decomposition into ammonia and hydrochloric acid, but these products recombine to ammonium chloride on cooling.

51. Ammonium Phosphates.—The most important of the compounds of ammonium and phosphorus is the *secondary ammonium sodium phosphate* or *microcosmic salt*, $\text{NH}_4\text{NaHPO}_4 \cdot 4\text{H}_2\text{O}$. It occurs in putrid urine and guano. It is prepared by mixing hot strong solutions of ammonium chloride and sodium phosphate, thus:



It forms large transparent, monoclinic crystals that are very soluble. When heated it boils violently, giving up water and ammonia, finally forming a transparent glass of sodium metaphosphate, which is used in blowpipe work for the detection of various metals.

LITHIUM

Symbol Li. Atomic weight 6.94. Valence I.

52. History and Occurrence.—Lithium oxide was recognized first as a new substance by Arfvedson, a Swedish chemist, in 1817. The metal was first prepared pure by Bunsen and Matthiessen in 1855. Lithium is a comparatively rare metal, being found principally in the rare minerals *amblygonite*, *spodumene*, *petalite*, *lepidolite*, and *triphylite*; the water of many mineral springs contains it in considerable quantity,

while traces of it have been detected by means of the spectroscope in sea-water, in many minerals and meteorites, as well as in various plants.

53. Preparation and Properties.—Metallic lithium is best obtained by the electrolysis of lithium chloride. On a large scale a mixture of potassium and lithium chlorides is electrolyzed. It is a brilliant, silver-white metal, somewhat softer than lead, and tarnishes in the air. It is remarkable as the lightest of the solid metals, having a specific gravity of only .5936. It melts at 180°C ., is ductile, and can be welded at ordinary temperatures, and burns in the air when more strongly heated. It bears a general resemblance to potassium and sodium, but it is harder and less easily oxidized than these metals. It decomposes water rapidly at ordinary temperatures, but does not burn on it. Its spectrum is characterized by an intense crimson line having a wave length of .0006705 millimeter.

COMPOUNDS OF LITHIUM

54. Some of the principal compounds of lithium are *lithium chloride*, LiCl , a deliquescent, fusible, and volatile salt; the *oxide*, Li_2O , and the *hydroxide*, LiOH , the latter a caustic, strongly alkaline substance; the *carbonate*, Li_2CO_3 ; the *sulphate*, Li_2SO_4 ; and the *phosphate*, Li_3PO_4 , all of which are well-defined salts.

RUBIDIUM

Symbol Rb. Atomic weight 85.45. Valence I.

55. Preparation and Properties.—Rubidium was first detected by Bunsen, in 1860, by means of the spectroscope. Its spectrum contains two characteristic dark-red lines, whence its name, which is derived from the Latin word *rubidus*, meaning *dark red*. It has since been found in small quantities in various mineral waters, and in the mineral lepidolite, as well as in the ashes of various plants. By distilling the carbonate with charcoal, rubidium is obtained as a soft, white metal with

a tinge of yellow, and a specific gravity of 1.52. It melts at 38.5°C . and volatilizes below a red heat. It is more easily oxidized than potassium, to which it is closely related. It burns on water with nearly the same colored flame as potassium. It is best preserved in hydrogen, and next to caesium is the most electropositive of all the metals. It dissolves in cold water, in acids, and in alcohol with great energy, evolving hydrogen.

COMPOUNDS OF RUBIDIUM

56. The salts of rubidium resemble closely those formed by potassium. The *chloride* crystallizes in cubes, dissolves in its own weight of water at 150°C ., and forms a double salt with platinum chloride. The *nitrate*, RbNO_3 , resembles in properties saltpeter, but crystallizes in hexagonal prisms. The *carbonate*, Rb_2CO_3 , is an alkaline deliquescent salt very soluble in water. The *sulphate*, Rb_2SO_4 , is isomorphous with potassium sulphate.

CÆSIUM

Symbol Cs. Atomic weight 132.81. Valence I.

57. Cæsium was discovered simultaneously with rubidium, and in the same mineral water. Its name is derived from the Latin word *cæsius*, meaning *sky blue*, and has reference to the two bright blue lines in its spectrum. It is widely distributed in small quantities in the rare mineral *pollux* as cæsium aluminum silicate, in many mineral springs, and in the ash of certain plants, as tobacco, tea, etc. Its specific gravity is 1.88. Cæsium is very similar to the other alkali metals, is a silver white, very soft, ductile metal, melting between 26°C . and 27°C . Heated in the air it burns rapidly, and takes fire when thrown on water. It is kept under petroleum, and is the most electropositive metal known. It is prepared by the electrolysis of a mixture of barium and cæsium cyanides, or by igniting the hydrate with aluminum in a nickel crucible.

GENERAL REVIEW OF THE GROUP OF ALKALI METALS

58. Cæsium, rubidium, potassium, sodium, and lithium constitute a group of elements conspicuous for their highly electropositive character, the powerfully alkaline nature of their hydroxides, and the general solubility of their salts. Their chemical characters and functions are directly opposite to those of the electronegative group embracing fluorine, chlorine, bromine, and iodine; and, like those elements, they exhibit a gradation of properties. Thus, cæsium appears to be the most highly electropositive member, rubidium the next, then potassium and sodium, while lithium is the least electropositive; and, just as iodine, the least electronegative of the halogen group, possesses the highest atomic weight, so cæsium, the least electronegative (or most electropositive) of the alkali metals, has a higher atomic weight than any other member of this group.

As in the case of the halogens, also, these are all univalent elements. Just as chlorine is accepted as the representative of *chlorous radicals*, so potassium is commonly regarded as the type of *basylous radicals*, the term *radical* being applied to all substances, whether elementary or compound, that are capable of being transferred, like chlorine or potassium, from one compound to another without suffering decomposition.

Attention has been called to the gradation of properties of the elements. In some of their salts a similar gradational relation may be observed; the carbonates, for instance, of cæsium, rubidium, and potassium are highly deliquescent, absorbing water greedily from the air, while carbonate of sodium is not deliquescent, and carbonate of lithium is only sparingly soluble in water.

FAMILY 1, GROUP B

GENERAL REMARKS

59. The relationship between the two groups of Family 1 is not very close, and the relationship between the members of Group B is not nearly as close as between the members of Group A. The members of Group B are not nearly so active chemically as those of Group A, but they form a greater variety of compounds. The members of Group A are univalent in all their salts, but all the members of Group B form some compounds in which their valence is greater than 1. *Copper* forms one series of salts in which it is monovalent, and one in which it is bivalent. *Gold* forms one series in which it is monovalent and one in which it is trivalent. *Silver* is nearly always univalent, but forms a few compounds in which its valence appears to be greater than 1. The chemical activity of the members of this group—copper, silver, and gold—decreases as the atomic weight increases.

COPPER

Symbol Cu. Atomic weight 63.57. Valence I and II.

60. **History and Occurrence.**—Copper has been known from the earliest times. The Romans obtained it from the island of Cyprus and called it *aes Cyprium*, a term that afterwards became *cuprum*, from which the English word *copper* is derived. It is found abundantly in nature, both free and in combination. Native copper occurs in masses of great size near Lake Superior; in Cornwall, England; in Siberia and the Ural Mountains, Russia. As cuprous oxide, Cu_2O , in the mineral *cuprite*, it is found in Cornwall, England, South America, and Australia; as cuprous sulphide,

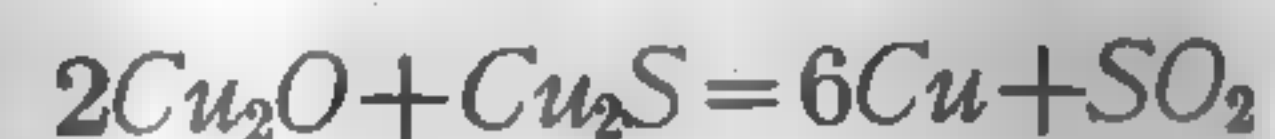
Cu_2S , in *copper glance*, and associated with sulphide of iron in *copper pyrites*; as *basic carbonate*, in *malachite*, $\text{Cu}_2(\text{OH})_2\text{CO}_3$; and in *azurite*, $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$. In addition to these minerals, which are used for the extraction of copper on a large scale, mineral silicates, phosphates, arsenates, and oxychloride are known. Copper is also found in the coloring matter of the red wing feathers of certain birds.

61. Preparation.—The method applied for the extraction of copper naturally varies with the ore under treatment. The oxides and carbonates are simply heated with charcoal or other fuel, with the addition of some silicious flux. The process of extracting copper from a mixture of copper sulphides and oxidized ore is a more complex operation, and a rather interesting one from a chemical point of view.

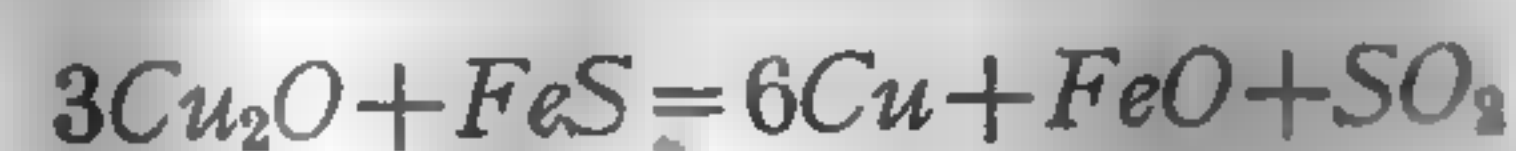
62. Chemical Reactions.—Copper possesses a greater affinity for sulphur and a smaller affinity for oxygen than the metals (especially iron) with which it is associated.

1. The ore is first moderately heated; part of the sulphur and arsenic is oxidized and passes off as sulphur dioxide and arsenic trioxide, respectively. This operation is regulated so that the sulphur retained is sufficient to combine with the whole of the copper to form cuprous sulphide, Cu_2S , the iron and part of the copper being transformed into oxide. The charge is then brought to a fusion at a higher temperature, when the ferrous oxide enters into combination with the silica, either originally contained in the ore or added to the charge to form a slag of ferrous silicate. By repetition of roastings and fusions the iron is thus ultimately removed.

2. At a moderate temperature the cuprous sulphide is then partly oxidized, and the temperature is raised so that the cuprous oxide formed may react with the sulphide:



The remainder of the sulphur is thus eliminated and metallic copper obtained. Any sulphide of iron that still remains is also acted on by the cuprous oxide as follows:



3. The crude copper so obtained is further refined by a process which is described in another article.

63. The Actual Operations.—1. *Calcination.*—This is performed either in heaps or on the bed of a reverberatory furnace. In the former the ore is made into heaps, the height of which varies according to the richness of the ore. The heat requisite is obtained by making a fire in the lower part of the heap, vents being provided so that a sufficient supply of air may be brought in contact with the ore. The main objects of this calcination are the removal of part of the sulphur and the volatilization, as completely as possible, of any arsenic or antimony present in the ore, as these substances are most prejudicial to metallic copper. If the calcination is carried out in a reverbera-

tory furnace, Figs. 4 and 5, the chief provisions to be attended to are a low temperature and properly regulated air supply admitted at A. The charge is introduced at the hoppers C, and spread over the bed of the furnace, being worked from the doors D, and finally withdrawn through openings E in the bed of the furnace, and shot down into the vault G, the course of the discharge exits is shown by dotted lines in Fig. 4.

2. *The Fusion.*—A high temperature is required for this process, which is carried out in a reverberatory furnace like the one shown in Figs. 4 and 5. At this stage ferrous oxide forms by double decomposition between ferrous sulphide and cuprous oxide, and this combines with silica, forming the slag, while the cuprous sulphide and the ferrous sulphide still remaining form the *matte*. The slag contains very little copper and is run off and thrown away, as it hardly pays to try to extract the little copper it contains.

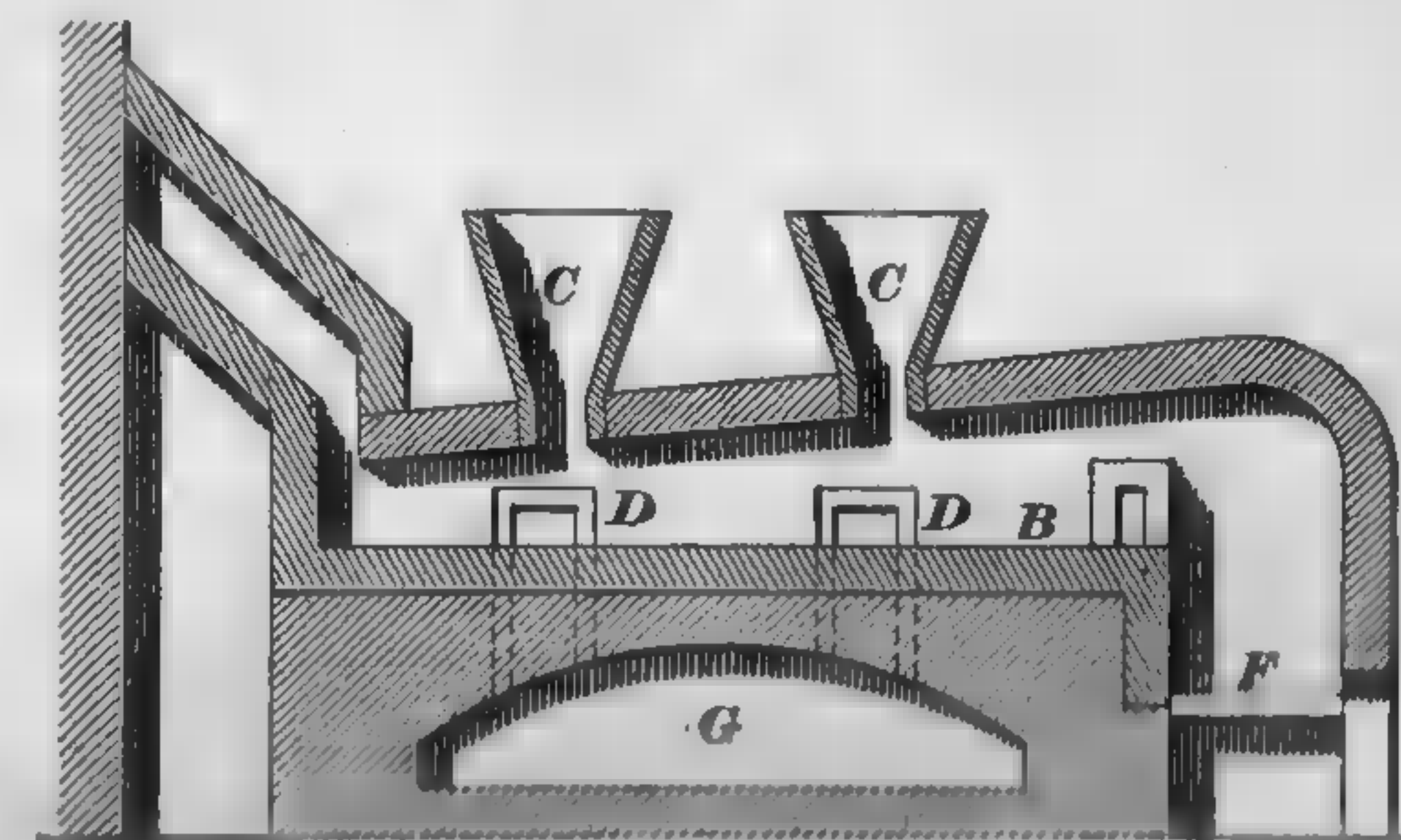


FIG. 4

The calcining and fusing operations are repeated several times, the matte becoming richer in copper each time.

3. *The Roasting.*—The object of the roasting is to partially oxidize the cuprous sulphide and induce the rest of the iron and other impurities that may still be contained in the matte to form a slag. It is performed in a reverberatory furnace with increased supply of air. When the oxidation has proceeded far enough, the temperature is raised so as to bring about the reaction between the cuprous oxide and the sulphide.

4. *The Refining.*—The crude copper, technically known as *blister copper*, is fused in an oxidizing atmosphere on the

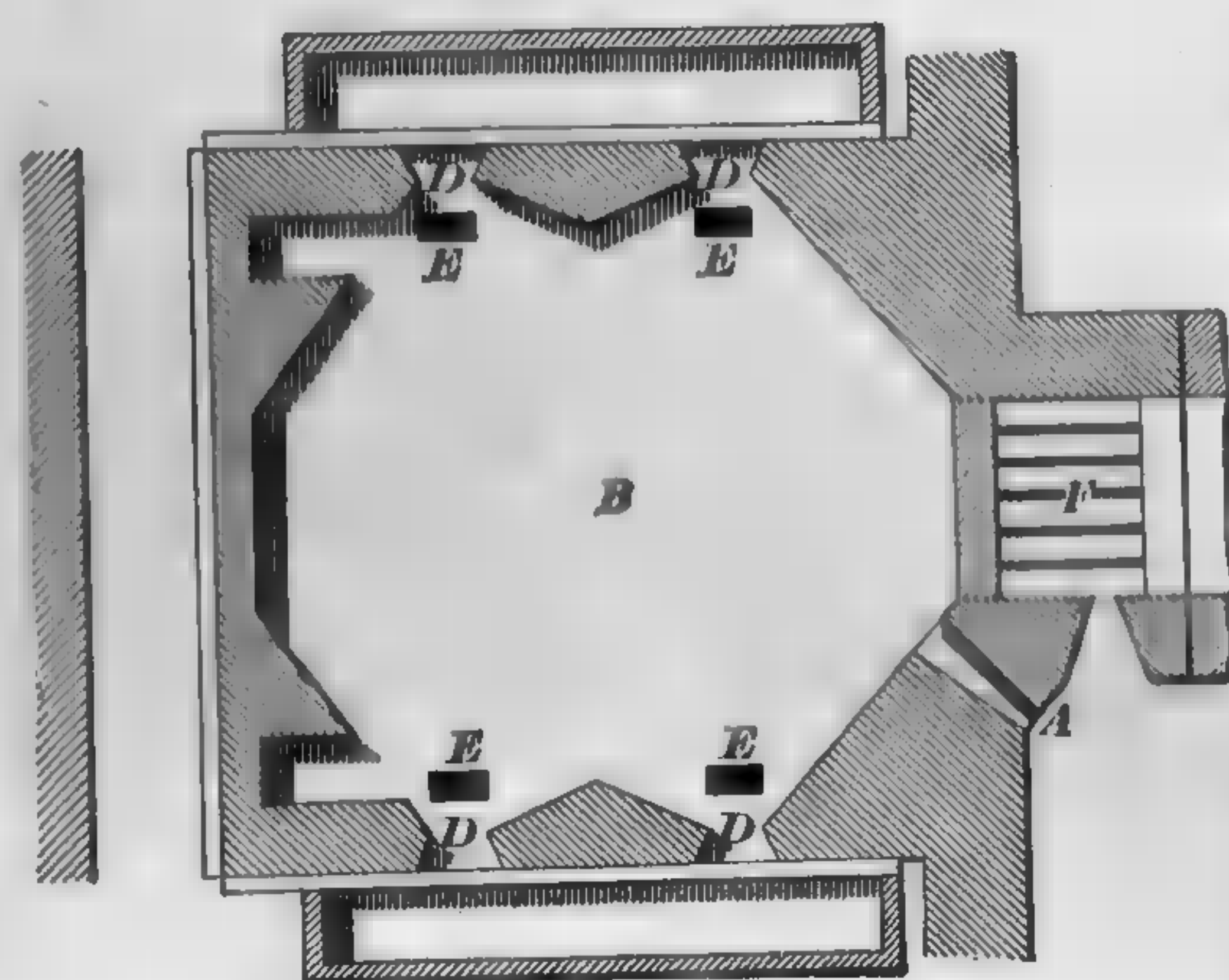


FIG. 5

bed of the refining furnace, and the still remaining impurities, such as arsenic, iron, antimony, sulphur, etc., are oxidized and skimmed off as slag. Finally, anthracite is sprinkled on the surface of the molten metal and the mass stirred with the trunk of a young tree, a process

known as *poling*. In this way the reduction of any remaining cuprous oxide is effected, and particles of slag are carried to the surface.

Perfectly pure copper is also obtained in this country by electrolytic processes.

Copper ores are also reduced in water-jacketed iron blast furnaces. The furnaces are elliptical in shape and are lined with firebrick. The roasted ore, coke, and slag, the latter consisting chiefly of iron silicate, is charged into the top of the furnace and air is forced in through tuyères near the bottom. This process forms a matte, which, with the slag formed, overflows into a forehearth. The slag, being lighter in specific gravity than the

matte, rises to the surface of the matte and flows from an opening in the upper edge of the forehearth. The matte is tapped from an opening at the bottom of the forehearth. This matte is then concentrated in another blast furnace and refined in the usual manner.

Sometimes the matte obtained from either of the preceding processes is charged into a Bessemer converter, where the foreign substances are removed by blowing air through the molten mass.

64. *Properties.*—Copper is a lustrous, sonorous metal of a peculiar red color and transmits a greenish blue light. Its specific gravity is 8.95, and it is somewhat softer than iron. When rubbed with the hand it exhales a peculiar, disagreeable odor. It crystallizes in isometric forms, and conducts heat and electricity very readily. It may be drawn into fine wire or beaten into thin leaves. Its tenacity is considerable, being next to iron. A copper wire 2 millimeters in diameter sustains a weight of 140 kilograms; it melts at 1080.5°C. , and may be volatilized by the heat of the oxy-hydrogen blowpipe. It is unaltered in dry air at ordinary temperatures, but it absorbs oxygen in the presence of moisture and carbon dioxide. Green spots then appear on the surface, constituting a basic carbonate of copper, which is the compound commonly known as *verdigris*. At a high temperature it absorbs oxygen very eagerly, being converted into black cupric oxide, if the oxygen is in excess; or into red cuprous oxide, if the metal is in excess. The oxidation of copper is accelerated if the metal is in a state of fine division; in fact, when very finely powdered it often takes fire spontaneously. Weak acids, alkalies, and saline solutions act on it slowly in the presence of air; hence, as all its salts are more or less poisonous, anything to be taken as food should not be prepared in vessels made of copper or any of its alloys.

Copper is much employed for the construction of boilers, stills, and worms. Owing to its high electric conductivity, enormous quantities of it are used in electric construction for cables, dynamos, etc. Sheet copper is used for coating the bottoms of ships, for roofing, etc.

65. Alloys of Copper.—Although pure copper is very ductile it does not make good castings, as it does not fill out the molds owing to its contracting unequally on cooling. The most important alloys of copper are given in Table I.

TABLE I
ALLOYS OF COPPER

Alloy	Constituents
Brass	3C, 1Z
White metal	35C, 13Z, 2.2T
Bronze coinage	95C, 1Z, 4T
Bell metal	3 to 4C, 1T
German silver	2C, 7.9N, 6.3Z, 6.5I
Cannon bronze	9C, 1T
Bronze	8.5C, 1T, 0.5Z
Phosphor-bronze	90C, 9T, 0.8P
Manganese bronze	7C, 3M

NOTE.— C=copper, Z=zinc, T=tin, I=iron, P=phosphorus, M=manganese.

COMPOUNDS OF COPPER

66. Copper forms two series of salts. It acts as a bivalent element in the principal series, which contains such well-known compounds as CuCl_2 , CuSO_4 , CuS , and CuO ; these are generally spoken of as *copper compounds*, though to distinguish them from the other series they are frequently called *cupric compounds*. Another series of salts, of which some of the members are apparently represented by the formulas CuCl , Cu_2O , Cu_2S , etc., is also known; these are called *cuprous compounds*. In this series, copper appears to be univalent, though it has been suggested that in these compounds copper is also bivalent, and that the formulas should be written Cu_2Cl_2 ,

$\text{Cu}-\text{Cl}$

etc., or $\begin{array}{c} | \\ \text{Cu}-\text{Cl} \end{array}$, etc. A determination of the vapor density of cuprous chloride seemed to point to the double formula, Cu_2Cl_2 ,

but the results were not conclusive, and so long as nothing definite is known of the composition of these compounds, it seems reasonable to use the simplest formula.

67. Cuprous oxide, Cu_2O , is found in nature, as *cuprite*, in either vitreous masses or red octahedral crystals. It is ordinarily prepared in the wet way by boiling a solution of copper acetate with glucose; a bright-red, crystalline powder is precipitated, which is anhydrous cuprous oxide. When heated in contact with air it absorbs oxygen and is converted into cupric oxide.

When potassium hydroxide is added to a solution of cuprous chloride, a yellow precipitate of cuprous hydroxide is thrown down. Cuprous oxide is used to impart a red color to glass.

68. Cupric oxide, CuO , occurs in nature as the mineral *melanconite*. It may be prepared by heating the metal in the air, or by calcining the hydrate, carbonate, or nitrate. It occurs in isometric forms—perhaps also in orthorhombic—but is generally massive. Its specific gravity is 6.3, and it fuses without change at a bright-red heat. Cupric oxide is easily reduced by both hydrogen and charcoal, with formation of either water or carbon dioxide, and hence is frequently used in organic analysis. It colors glass a beautiful emerald green. *Cupric hydrate, $\text{Cu}(\text{OH})_2$,* is thrown down as a pale-blue precipitate on adding sodium hydrate to a cold solution of a cupric salt. It is strongly basic and forms numerous salts.

69. Cupric Sulphide and Cuprous Sulphide.—*Cupric sulphide, CuS ,* is found in nature as the mineral *covellite*. It is hexagonal in its crystallization, is of bluish-black color, and semimetallic luster, and has a specific gravity of 4.6. It is the black precipitate obtained when copper salts are precipitated by hydrogen sulphide. *Cuprous sulphide, Cu_2S ,* also occurs in nature, forming the mineral *chalcocite*. It may be prepared by exposing finely divided copper or copper foil to sulphur vapor. It crystallizes in orthorhombic prisms, is blackish gray in color, has a metallic luster which is frequently tinged with green, and is easily fusible.

Copper also forms two series of haloid salts, the cuprous CuF , CuCl , and the cupric CuF_2 , CuCl_2 , etc. These latter haloid salts, though in general tolerably stable in solution, and obtainable therefrom on concentration in crystals, are readily decomposed by heat and converted into the cuprous form, in which they are insoluble in water. The cupric iodide, however, breaks up even in the moist condition, and the precipitate obtained on adding potassium iodide to solutions of cupric salts, consists of white cuprous iodide and iodine. Cuprous salts give, under the same circumstances, a pure white precipitate of cuprous iodide.

70. Cuprous chloride, CuCl , is formed by burning copper in chlorine or by the action of reducing agents, such as sulphurous acid, zinc dust, or metallic copper, on cupric chloride. If, therefore, cupric oxide is dissolved in concentrated hydrochloric acid, the solution when boiled with excess of copper contains cuprous chloride, which is deposited as a white powder when it is poured into a large quantity of water. This, on exposure to air, turns green, owing to the formation of a basic chloride. The solution of cuprous chloride absorbs carbon monoxide and is used for determining the amount of this gas in certain gaseous mixtures; in presence of acetylene, C_2H_2 , a basic cuprous acetylide is formed, from which pure acetylene may be liberated by treatment with acid.

71. Cupric chloride, CuCl_2 , is formed when metallic copper or cuprous chloride is heated in excess of chlorine. It crystallizes in green needles with 2 molecules of water. It is obtained as a green solution by digesting cupric oxide with concentrated hydrochloric acid, and adding water.

72. Cupric sulphate, CuSO_4 , more commonly known as *copper sulphate* or *blue vitriol*, can be prepared by treating almost any cupric compound, as the hydroxide, carbonate, etc., with sulphuric acid. It is frequently prepared on a large scale by treating cupric sulphide with sulphuric acid. The simplest process consists in boiling copper turnings and clippings with sulphuric acid, sulphur dioxide being disengaged

and cupric sulphate formed. In the arts, the operation is conducted in lead-lined wooden tanks heated by steam.

Cupric sulphate crystallizes in large, blue, prismatic crystals that contain 5 molecules of water. When exposed to dry air, they effloresce superficially; heated to 100° they lose 4 molecules of water, disengaging the fifth only at 220°C. to 260°C. The anhydrous salt is white. At a high heat, cupric sulphate is decomposed into cupric oxide, sulphur dioxide, and oxygen. Cupric sulphate dissolves in 4 parts of cold and 2 parts of boiling water, and the concentrated solution has a pure blue color. It is insoluble in alcohol.

When an excess of ammonia is added to a solution of cupric sulphate a beautiful, dark-blue liquid is obtained. It contains ammoniacal cupric sulphate, $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, which separates as dark-blue crystals when alcohol is added to the aqueous solution.

There are several basic sulphates of copper representing compounds of cupric sulphate and cupric hydrate. One of them is obtained as a green powder when a solution of cupric sulphate is digested with cupric hydrate. The bluish precipitates obtained by incompletely precipitating solutions of cupric sulphate with potassium hydrate are basic sulphates.

Cupric sulphate is employed as a caustic applicable to diseases of the eye. In the arts, it is used in the preparation of *blue ashes*, a mixture of calcium sulphate and cupric hydrate, made by decomposing cupric sulphate with milk of lime. It is much used in dyeing, particularly in dyeing black on wool and cotton; it is also employed for preserving wood. Large quantities of sulphate of copper are employed for electrotyping and electric batteries.

73. Carbonates of Copper. When cold solutions of sodium carbonate and cupric sulphate are mixed, a bluish-green precipitate is obtained, and at the same time carbon dioxide is disengaged. The precipitate becomes green when washed with warm water. It is known as *mineral green*, and can be regarded as a combination of 1 molecule of cupric carbonate with 1 molecule of cupric hydrate. It contains:



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A similar compound exists in nature, constituting *malachite*. This mineral occurs in green masses. When cut and polished, it presents veins of various tints, and is fashioned into ornamental objects. Verdigris has the same composition.

Azurite, or *mountain blue*, which crystallizes in beautiful, blue, oblique rhombic prisms, can be regarded as a compound of 2 molecules of cupric carbonate with 1 of the hydrate:



SILVER

Symbol Ag. Atomic weight 107.88. Valence I:

74. History and Occurrence.—Silver has been known in the metallic form from the earliest historic times. The ancient alchemists gave to it the name of Luna from its bright white color.

It is found in a free state in the United States, Mexico, Peru, and many other countries. Its most important ores are *argentite*, Ag_2S ; *pyrargyrite*, Ag_2SbS ; and *horn silver*, AgCl . It is found also in combination with lead sulphide, copper sulphide, and many other ores.

75. Préparation.—The process employed for the extraction of silver varies, naturally, with the quality of the ore. At Freiberg, in Germany, the ore—an impure sulphide—is roasted with 10 per cent. of salt; the resulting mass is ground to a fine powder, and agitated in revolving barrels containing water and scrap iron, by which the silver is reduced to the metallic state. Mercury is then added to dissolve the silver, and by distilling the amalgam thus obtained the silver is left pure. In this country most of the silver is obtained in the lead-smelting process, or in connection with gold, by amalgamation, or one of the lixiviation processes.

The most common method employed in the United States consists of mixing the silver ore with other ores rich in lead and smelting this mixture with iron (either as scrap or as iron ore), limestone, and coke in a blast furnace. The silver-lead alloy

obtained (base bullion) usually contains gold, some copper, antimony, bismuth, etc. The base bullion is melted and then allowed to cool almost to the point of solidification, when the copper, bismuth, antimony, etc. rise to the top of the molten mass and are skimmed off. The greater portion of the lead in the base bullion is then removed either by melting the mass and allowing it to cool slowly when pure lead crystallizes out, or by adding zinc to the molten mass and cooling. An alloy of lead-silver zinc, rich in silver, now rises to the surface and is skimmed off. The zinc is expelled by distillation and the lead removed by cupellation. Any gold obtained in the base bullion will be found with the silver after cupellation.

76. Properties.—Pure silver is a remarkably white, lustrous metal of specific gravity 10.5, and capable of taking a high polish. It is the best known metallic conductor of heat and electricity, is harder than gold, and is very ductile and malleable, although working of silver hardens it and it must be softened repeatedly by heating to a dull redness. It crystallizes in regular octahedra, melts at 961.5°C. , and may be distilled at the highest temperature of the oxyhydrogen blowpipe. When melted, silver is capable of absorbing twenty-two times its own volume of oxygen, which, however, is again evolved when it solidifies. It is unaltered in the air at any temperature, though it is readily acted on by chlorine, sulphur, and phosphorus. It is readily soluble in nitric acid, but difficultly soluble in hydrochloric and sulphuric acids. The alkalis have no action on it; for this reason silver vessels are used in the laboratory for fusing potassium hydrate and concentrating its solutions. By the action of certain reducing agents on silver salts, the metal is obtained in a finely divided condition, in which form it shows brilliant golden, ruby, blue, and other colored tints.

77. Uses.—Owing to its softness, silver is rarely used in the pure state. It is generally alloyed with copper, which, while it greatly increases its hardness, scarcely alters its color. The silver-coin alloy of the United States and France contains 10 per cent. of copper, that of England 7.5 per cent., and that

of Germany 12.5 per cent. The silver used in silver plate usually contains from 70 to 95 per cent. of pure silver.

The operation of *silvering*, as its name indicates, consists in covering the common metals or glass with a coating of silver of greater or less thickness. The metals are silvered by either amalgamation or galvanic deposition. In the latter and much more preferable operation, a solution of the double cyanide of silver and potassium is generally used.

Mirrors and glass articles in general are silvered by the reduction of a silver salt by aldehyde, glucose, or tartaric acid. The following recipe is given by *Liebig*: A solution of 10 grams of silver nitrate is supersaturated with ammonia and sodium hydroxide is added; the volume of the liquid should be 1,450 cubic centimeters. Another solution is prepared by dissolving 1 part of milk sugar in 10 parts of water. This solution is mixed with its own volume of the first solution, and the glass to be silvered is washed with alcohol and immersed in the liquid. The reduction of the silver salt begins immediately, and does not require the aid of heat.

The experiment may be easily made in a small glass flask, the interior of which will be uniformly silvered.

Electroplating consists of covering the surface of baser metals with a coating of silver, by connecting them with the negative (or zinc) pole of the galvanic battery, and immersing them in a solution made by dissolving silver cyanide in potassium cyanide (a solution of potassium cyanide in 10 parts of water, with 3.5 grams of silver chloride dissolved in each pint of the liquid, will answer the purpose nicely), the positive (copper or platinum) pole being connected with a silver plate, also immersed in the solution. The electric current gradually decomposes the silver cyanide, and this metal is deposited on the object connected with the negative electrode, while the cyanogen liberated at the silver plate attacks the silver, so that the solution is always maintained at the same strength; the quantity of silver dissolved at this electrode is precisely equal to that deposited at the opposite one.

COMPOUNDS OF SILVER

78. Silver oxide, Ag_2O , is usually prepared by adding a strong, hot solution of silver nitrate to one of potassium hydroxide. It is a dark-brown powder with a specific gravity of 7.2. It is readily decomposed by heat, and partly decomposed by light, into metallic silver and oxygen. It is only slightly soluble in water when freshly prepared; ammonia dissolves it readily, the solution depositing a violently explosive crystalline compound. *Silver hydroxide, $AgOH$,* is a strong base, is alkaline, and becomes silver oxide on heating to $60^\circ C$.

79. Silver Sulphide.—To the oxide of silver corresponds the **sulphide, Ag_2S ,** which occurs in nature as *silver glance*, or *argentite*, crystallized in regular octahedrons. It is soft, and can be scratched with the finger nail. It is prepared either by heating together silver and sulphur or by precipitating silver salts with hydrogen sulphide.

80. Silver fluoride, AgF , is formed when the oxide or carbonate is dissolved in hydrofluoric acid. It is soluble in little more than half its weight of water, the solution having a strongly alkaline reaction. The salt takes up about 840 times its volume of ammonia.

81. Silver chloride, $AgCl$, occurs in nature as the mineral *cerargyrite*. It may be obtained by the direct union of silver and chlorine or by precipitating a solution of silver nitrate by a chloride. A white, curdy mass, soluble in ammonium hydrate, but insoluble in nitric acid, is thrown down, which, on drying, becomes a white powder. When heated to $470^\circ C$., it fuses to a dark-yellow liquid, and on cooling solidifies to a translucent, sectile mass resembling horn, whence the name *horn silver*, sometimes applied to it. It has a specific gravity of 5.5, crystallizes in isometric forms, and turns black on exposure to light. For the latter reason it is used in photography.

If recently precipitated and moist silver chloride is placed on a sheet of zinc, in a short time a dark color will appear on the borders of the chloride, and the whole of that body will soon be converted into a dark-gray powder of finely divided

silver, zinc chloride being at the same time formed. This reaction takes place much more rapidly if the silver chloride is moistened with hydrochloric acid; in which case the reduction is effected by nascent hydrogen produced by the action of the hydrochloric acid on the zinc.

82. Silver bromide, $AgBr$, and silver iodide, AgI , are both found in nature in Mexico and Chile. Silver bromide may be obtained on adding hydrobromic acid, or a bromide of an alkali metal, to a solution of silver nitrate, as a yellowish-white, curdy precipitate, which is insoluble in nitric acid and nearly so in dilute ammonia—whereby it is distinguished from silver chloride, and melts at $426^{\circ}C.$, forms a reddish liquid. When suspended in water it is easily decomposed by chlorine; hydrochloric-acid gas also decomposes it at $700^{\circ}C.$ with the evolution of hydrobromic acid. The precipitated bromide, when exposed to light, changes its color and assumes a grayish tint.

Silver iodide is a yellow, insoluble precipitate, produced by adding silver nitrate to potassium iodide. It is insoluble or, nearly so, in ammonia, and in this respect forms an exception to silver salts in general. It blackens on exposure to light, melts at $555^{\circ}C.$ to a yellow liquid, which becomes brown on continued heating.

83. Silver nitrate, $AgNO_3$, or lunar caustic, is prepared by dissolving pure silver in nitric acid and allowing it to crystallize, or the solution is evaporated and the residue fused and cast into sticks. It crystallizes in rhombic tables or plates that melt at $218^{\circ}C.$, have a specific gravity of 4.3, and are readily soluble in alcohol and water. It is dimorphous, is odorless, has a bitter, metallic taste, and a caustic action, rapidly blackening and destroying organic matter. It does not blacken in the air unless organic matter is present. Thus it stains the fingers black when exposed to the light, but the stain may be removed by potassium cyanide, or, more safely, by tincture of iodine.

Silver nitrate is used in photography, in medicine, and to some extent in marking inks for linen and cotton goods, since

the deposit of metallic silver formed on exposure to the light is not affected by washing.

84. Silver nitrite, $AgNO_2$, was first obtained by Proust. It is prepared by mixing warm solutions of silver nitrate and potassium nitrite. On cooling, silver nitrite separates in white crystalline needles slightly soluble in water, and decomposing, without fusion, when heated to $180^{\circ}C.$ It dissolves in boiling water with partial decomposition.

85. Silver sulphate, Ag_2SO_4 , is the final product obtained when silver sulphide is roasted in the air. It is also prepared by dissolving metallic silver in hot sulphuric acid. It crystallizes in small rhombic prisms that are isomorphous with anhydrous sodium sulphate. It is difficultly soluble in water, fuses at $654^{\circ}C.$, and decomposes at a high temperature.

86. Silver sulphite, Ag_2SO_3 , is precipitated as a white curdy mass when sulphurous acid is added to a solution of silver nitrate. It is insoluble in water, blackens in the light, and decomposes at $100^{\circ}C.$

87. Silver orthophosphate, Ag_3PO_4 , is formed as a yellow precipitate when a solution of sodium orthophosphate is added to a solution of silver nitrate. It is soluble in nitric acid, but insoluble in water. It is affected by the light, turns brown on heating, and melts at a red heat. It is used in photography.

88. Silver arsenite, Ag_3AsO_3 , and silver arsenate, Ag_3AsO_4 .—The former salt is obtained as a yellow precipitate insoluble in water and alcohol when a mixture of the solutions of silver nitrate and arsenious acid is made just ammoniacal in the cold. If this solution is boiled metallic silver separates. It is soluble in an excess of ammonium hydrate. The arsenate is obtained as a reddish-brown precipitate when silver nitrate is added to arsenic acid. It is soluble in nitric acid and ammonium hydroxide.

GOLD

Symbol Au. Atomic weight 197.2. Valence I and III.

89. Occurrence and Preparation.—Gold occurs widely distributed in nature, though in small quantity, as a rule. It is almost always found in the metallic state, usually associated, however, with certain quantities of silver, copper, or iron, and also in special ores, with bismuth and tellurium. Many minerals, such as galena, iron pyrites, and zinc blende, contain traces of gold. Though one of the rare metals, it is widely distributed; the chief localities where it is mined are the Rocky Mountain and Pacific Coast States in this country, Australia, South Africa, and the Klondike. It is found generally in quartz veins intersecting metamorphic rocks of various ages, and in the alluvial detritus (gravel) that has resulted from the disintegration of these rocks. Partly in consequence of the value of the metal, and partly from the simplicity of the methods by which it is worked, a deposit containing as little as 1 part of gold in 500,000 may sometimes be profitably worked. To extract gold from auriferous quartz, the whole is first powdered roughly by mechanical means, and then subjected to separation in sluices, so arranged that the heavier particles containing the gold collect at the bottom of the sluice, while the gangue is carried off by the stream of water. The gold is separated by causing it to form an amalgam with mercury, or to collect on amalgamated copper plates. The mercury is finally distilled off, leaving the gold behind as residue.

In the *chlorination process* the ore (iron pyrites or sulphide concentrates from stamp mills) is roasted, so that the iron is transformed into ferric oxide, which is not readily attacked by moist chlorine, and then subjected to the action of chlorine. The gold is thus converted into chloride, which can be dissolved out in water, and metallic gold precipitated from the solution by the addition of reducing agents, such as ferrous sulphate.

Potassium cyanide is now largely used for extracting gold, as it readily dissolves in this reagent.

The separation of silver and copper from gold may be effected by *quartation*, the success of which, as the name implies, depends on the gold being present to the extent of not more than one-quarter of the mass of metal employed. The metal is boiled with strong sulphuric acid, and the silver and copper are thus converted into sulphates, so that on lixiviation with water these are dissolved and the gold left as residue.

90. Properties.—Gold is a soft, orange-yellow metal of great brilliancy. Its physical character renders it very conspicuous among the metals; it is the heaviest of metals in common use, with the exception of platinum, its specific gravity being 19.43. In malleability and ductility it surpasses all other metals; the former property is turned to advantage for the manufacture of gold leaf, for which purpose a bar of gold, containing 96.25 per cent. of gold, 2.5 per cent. of silver, and 1.25 per cent. of copper, is passed between rollers that extend it into the form of a broad ribbon; this is cut into squares that are packed between layers of fine vellum, and beaten with a heavy hammer; these thinner squares are then again cut up and beaten between layers of gold-beater's skin until they are sufficiently thin. An ounce of gold may thus be spread over 100 square feet; 282,000 of such leaves placed on one another form a pile of only 1 inch high. The gold leaves transmit green light, though when rendered non-lustrous by heat this light is ruby red.

Although fusing about the melting point of copper, gold is seldom cast, on account of its great contraction during solidification. Gold crystallizes in isometric forms, conducts heat and electricity well, and fuses at $1,061.7^{\circ}\text{C}$. It is unaltered in the air, and is not attacked by any single acid or alkaline hydroxide, though solutions that contain free chlorine, like aqua regia, dissolve it readily.

Gold is used both for jewelry and coinage. Being too soft, alone, for either purpose, it is alloyed with copper or silver, the mint alloy of the United States consisting of 9 parts of gold and 1 of copper. The purity of gold for jewelry is estimated by the *carat*, pure gold being 24 carats fine; hence, an alloy of 18 parts of gold to 6 of silver and copper is said to be 18 carats fine.

91. Gilding.—Gold is not even affected to the same extent as silver by exposure to the atmosphere, for hydrogen sulphide has no action on it, and hence is better adapted than any other metal for coating surfaces that are required to preserve their luster.

Several processes are used for gilding metals, such as silver and copper. The objects may be gilded by amalgamation, or by galvanic deposition. Gold readily alloys with mercury, and the amalgam is used for gilding objects of silver and copper. The pieces to be gilded are heated to destroy greasy matters, and are then cleaned by dipping them into dilute sulphuric acid, after which they are washed, and dried with sawdust. They are then rubbed with a brush of brass wires dipped into a solution of mercurous nitrate, and then with a brush impregnated with an amalgam of 1 part of gold and 8 parts of mercury. They are afterwards heated to volatilize the mercury. The pieces thus gilded are dull; they become lustrous after suitable washings and polishings.

The best process of gilding is the electrogilding. In this process the copper objects, previously heated and cleaned by dilute sulphuric acid, are plunged for a few seconds in dilute nitric acid and then wiped dry. They are then connected with the negative pole of a battery and dipped into a bath composed of 1 part of cyanide of gold, 10 parts of potassium cyanide, and 100 parts of water. A plate of gold plunged into the same bath constitutes the positive pole. When the current passes, the objects become covered with a uniform and adherent coating of gold. As the metal is precipitated from the solution, it is replaced by an equivalent quantity from that which constitutes the positive pole, and which dissolves. The bath thus retains a constant composition. Best results are obtained when the solution is hot.

COMPOUNDS OF GOLD

92. Oxides of Gold.—Three compounds of gold and oxygen are known, namely: Au_2O , Au_2O_3 and a auro-auric oxide $(AuO)_4$.

Aurous oxide, Au_2O , is a violet-colored powder obtained when aurous chloride is treated with potassium hydroxide. Hydrochloric acid forms metallic gold and the trichloride, thus:



Heated to 250° C. it decomposes into gold and oxygen. Sulphuric acid and nitric acid do not affect it.

Auric oxide, Au_2O_3 , is obtained as a brown powder by gently heating auric hydroxide, obtained by treating a hot solution of auric chloride with a hot solution of sodium hydroxide and adding sodium sulphate. Heat decomposes this oxide into metallic gold and oxygen. It is soluble in nitric acid. Potassium hydroxide dissolves it, forming *potassium aurate*, $KAuO_2$.

93. Chlorides of Gold.—*Auric chloride*, $AuCl_3$, is formed when gold is dissolved in aqua regia, and if this solution is evaporated, the auric chloride is partly decomposed, with the formation of *aurous chloride*, $AuCl$. It is formed also by passing chlorine gas through water containing finely divided gold in solution. It melts at 288° C., when heated in a sealed tube. Auric chloride may be obtained in crystals containing 2 molecules of water of crystallization, $AuCl_3 \cdot 2H_2O$. When a solution of auric chloride is treated with stannous chloride a purple precipitate, known as *purple of Cassius*, is formed. This appears to be metallic gold in a finely divided condition. When dry auric chloride is gently heated, it is decomposed into chlorine and aurous chloride, and if this is treated with water it is decomposed into auric chloride and gold.

94. Sulphides of Gold.—*Auric sulphide*, Au_2S_3 , is precipitated from a cold solution of a gold salt by hydrogen sulphide, as a black or brownish-black mass, which is accompanied by free sulphur. This sulphide is very unstable, and forms soluble compounds when treated with alkaline sulphides.

Aurous sulphide, Au_2S , is precipitated as a steel-gray substance when a hot solution of a gold salt is treated with hydrogen sulphide. This sulphide dissolves in pure water, and is reprecipitated from this solution by hydrochloric acid.

INORGANIC CHEMISTRY

(PART 9)

FAMILY 2, GROUP A

GENERAL REMARKS

1. Family 2, Group A, consists of the elements *glucinum*, *magnesium*, *calcium*, *strontium*, *barium*, and *erbium*. Calcium, strontium, and barium are not only very closely related to one another, but in some ways they are related to the members of Family 1, Group A (known as the alkalies), and in some ways to Family 3, Group A (known as the earth metals); they are frequently called the metals of the alkaline earths. Glucinum and magnesium are very closely related to each other, to the elements composing the alkaline earths in some ways, and to the elements in Family 2, Group B. The alkaline earths are much more closely related to one another than to the first two members of this group. Sometimes this group is subdivided into the *calcium subgroup*, consisting of barium, strontium, and calcium, and the *magnesium subgroup*, consisting of glucinum and magnesium.

The position of erbium in the periodic system is not firmly established. Its atomic weight is now generally accepted as 167.7, which, if correct, would place it in Family 2. Its oxide apparently has the composition Er_2O_3 , which would indicate that it belongs in Family 3. It has recently been shown that some of the substance believed to be erbium consisted, in part at least, of the oxides of other rare elements. The fact that it

occurs in very complicated minerals renders its study difficult, and at present it has not been studied so thoroughly that anything in regard to it can be stated with absolute certainty.

The alkaline earths are the most prominent members of this group, and as calcium is the most abundant and important member of these it will be discussed first.

CALCIUM

Symbol Ca. Atomic weight 40.07. Valence II.

2. History and Occurrence.—Calcium carbonate and sulphate were known to the ancients, the former being burned into lime for making mortar. It is from the Latin word for lime, *calx*, that the name calcium has been derived. The metal itself was discovered by Davy in 1808 and isolated in 1855 by Matthiessen, who obtained it by decomposing fused calcium chloride by means of the voltaic current. It is found abundantly in the mineral kingdom. As carbonate it forms the mineral calcite and the rock masses known as *limestone*, *chalk*, and *marble*. As sulphate, it forms vast beds of *gypsum*; as phosphate, it occurs as *apatite*; as fluoride, in *fluorspar*, etc. It also occurs as the phosphate in the bones of animals, in the shells of eggs and oysters, and in nearly all spring and river waters.

3. Preparation and Properties.—Metallic calcium may be obtained by the electrolysis of the fused chloride, or by heating an alloy of zinc and calcium to a high temperature to distil off the zinc and leave the calcium. The alloy is prepared by fusing together a mixture of calcium chloride, zinc, and sodium, when the sodium decomposes the chloride, and the calcium and zinc form an alloy; also, by the reduction of the oxide by heating with magnesium. Metallic calcium has a light-yellow, brilliant color, is about as hard as gold, and is very ductile and malleable. It oxidizes slowly in the air, though it is permanent in perfectly dry air. It decomposes water at ordinary temperatures. Its specific gravity is 1.57. The salts of calcium impart a brick-red tinge to an otherwise colorless flame.

COMPOUNDS OF CALCIUM

4. Calcium oxide, CaO , commonly known as *lime* or *quicklime*, is always prepared on a large scale by igniting its carbonate. This operation is conducted in a rather rude furnace of masonry, called a *kiln*, which is usually located adjacent to the side of the hill containing the limestone quarry, as shown in Fig. 1. The stone is hauled over a platform built from the

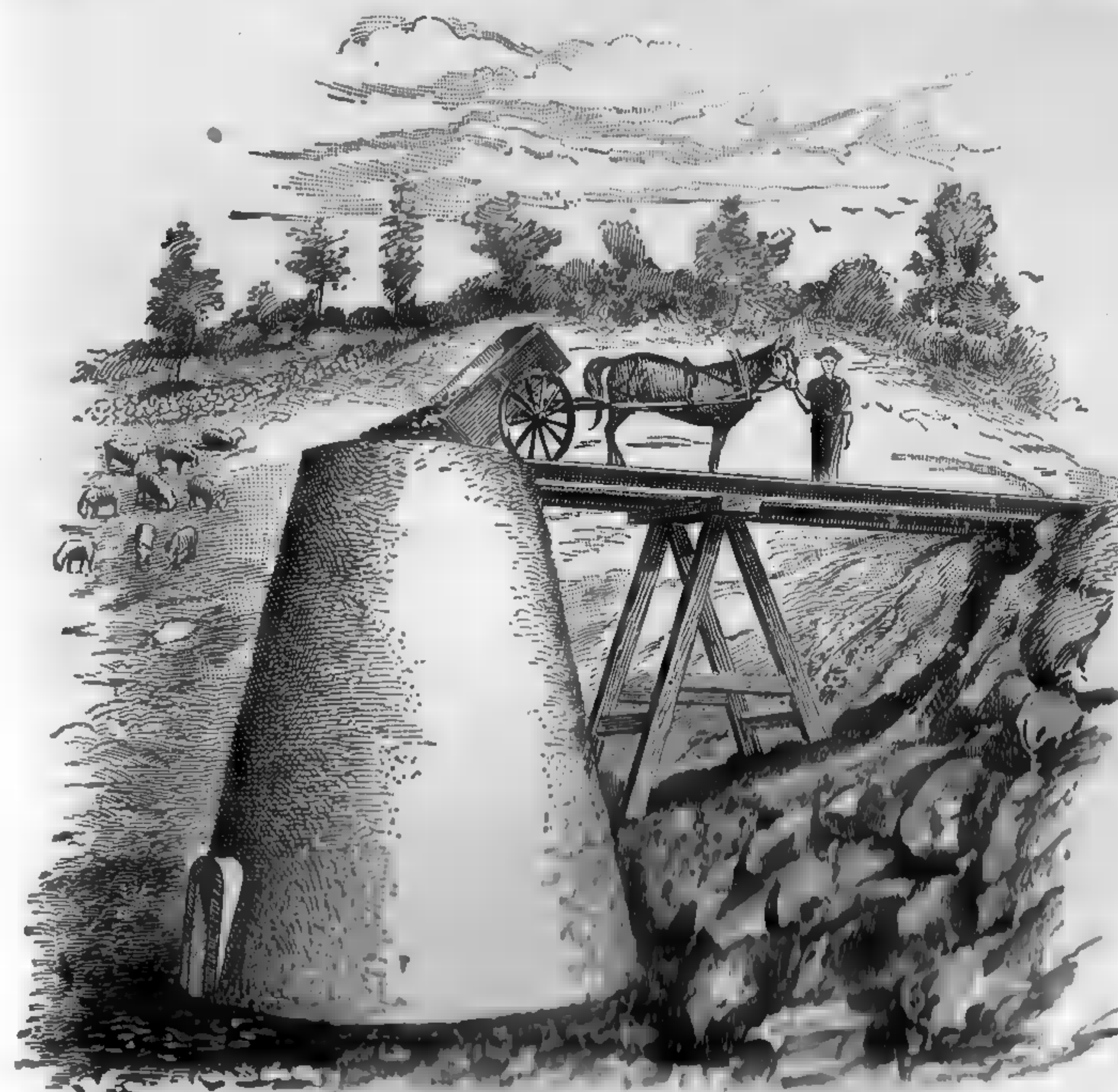


FIG. 1

hill and dumped into the top of the kiln, in which an opening is left, not only for charging, but as an exit for the gases and smoke evolved during the process of burning. The *charge*, as the quarried limestone is called when placed in the kiln, rests on an arch built on the hearth with large pieces of limestone. It is piled up nearly to the top of the kiln, as shown in Fig. 2. The fire is built on the hearth, and lighted near the back, so

that it will become more intense toward the mouth as the draft increases. The air that enters by the firedoor carries the flame to all parts of the arch, and gradually brings the limestone to a state of white heat.

Fig. 2 shows the section of the conical lime kiln usually built in this country; *a* shows the limestone arch that rests on the firebrick hearth *b*, and under which the fire is built; *c* is the loose limestone thrown around and over the arch *a*, and is composed of smaller pieces of rock; *e* is the inside, firebrick, lining of the kiln; *f* is the wall of the kiln itself, built of either stone or brick; *g* is the outside coating or plastering of clay, put on to keep as much of the heat in the kiln as possible; *h* is the upper opening, through which the kiln is charged, and which also acts as a chimney for the escape of smoke, etc.; *j* is the wood fire that produces the necessary heat.

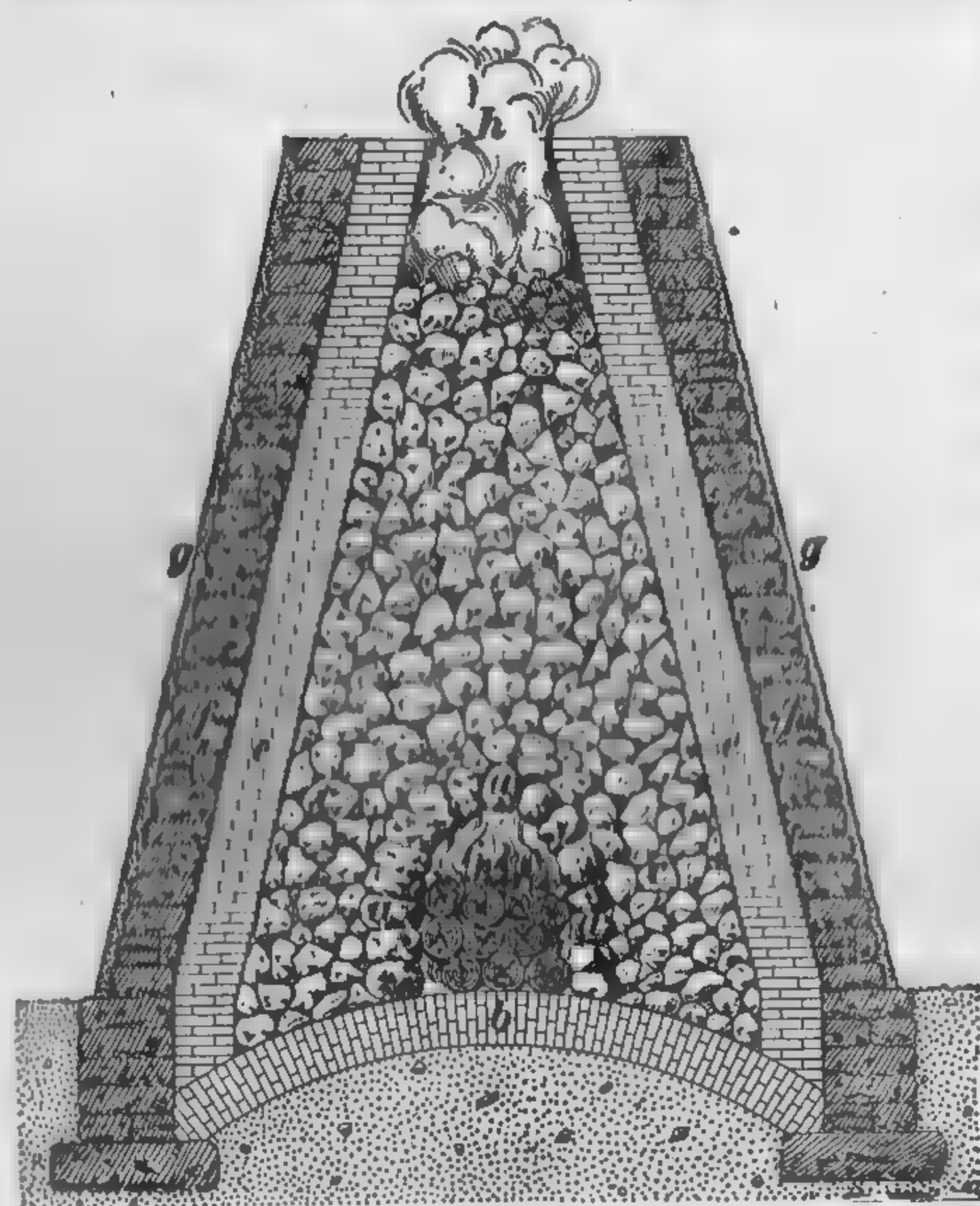


FIG. 2

It is a strong base, is non-volatile, melts at 780° to 800° C., the vapor condensing to cubical crystals with a specific gravity of 3.4. On exposure to the air, calcium oxide combines with the moisture of the air and crumbles. It absorbs water with great rapidity, forming the hydroxide and generating considerable heat. Calcium oxide is soluble in acids and slightly soluble in water, about 1 part in 800 parts of water.

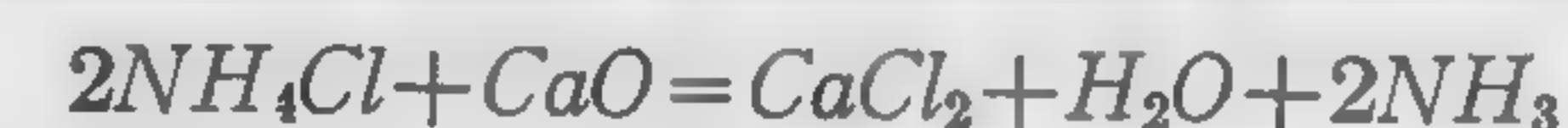
5. Calcium hydroxide, $\text{Ca}(\text{OH})_2$, is obtained by slaking lime; that is, by adding water to CaO . It is a soft, white,

bulky powder, and is slightly soluble in water, forming an alkaline, feebly caustic liquid known as *lime water*. Lime water readily absorbs CO_2 from the atmosphere, becoming milky, and precipitates CaCO_3 . Calcium hydroxide is easily converted into calcium oxide by heat. It is widely used in manufacturing chemistry, being the cheapest alkaline substance.

Pure calcium oxide is a white hard amorphous substance having a specific gravity of about 3.

bulky powder, and is slightly soluble in water, forming an alkaline, feebly caustic liquid known as *lime water*. Lime water readily absorbs CO_2 from the atmosphere, becoming milky, and precipitates CaCO_3 . Calcium hydroxide is easily converted into calcium oxide by heat. It is widely used in manufacturing chemistry, being the cheapest alkaline substance.

6. Calcium chloride, CaCl_2 , is produced by dissolving either calcium oxide or carbonate (chalk or white marble, for instance) in hydrochloric acid, and is frequently obtained as a waste product in the chemical arts, as in the manufacture of ammonia from ammonium chloride and quicklime:

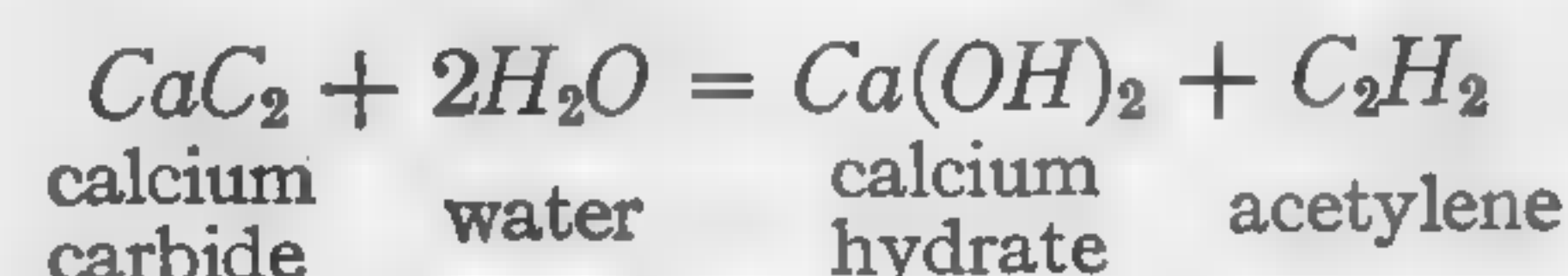


On evaporating a solution of calcium chloride in water, prismatic crystals of the composition $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ are obtained. These crystals, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, lose 2 molecules of water when dried in vacuo, and the whole 6 molecules when heated above 200° C. The calcium chloride thus obtained, free from water, is used as a drying agent in the laboratory, as it possesses a great eagerness to combine again with water. In consequence of the attraction of calcium chloride for water, surfaces wetted with a solution never get dry, and this solution is, consequently, frequently employed to make mantelets, for the protection of gunners, and also to render various objects, such as ropes, scenery, etc. in theaters, reasonably fireproof.

The crystals of calcium chloride are used with snow as a freezing mixture; in it a thermometer falls to -48.5° C. Calcium chloride melts at a full red heat, and if heated in the air evolves chlorine. A saturated solution of calcium chloride boils at 180° C., and is sometimes used in the laboratory as a convenient bath for obtaining a temperature above the boiling point of water.

7. Calcium carbide, CaC_2 , is obtained, according to Moissan, a French chemist, in the following way: At the high temperature of the electric furnace, lime is promptly reduced by carbon, but metallic calcium is not obtained. The reduced metal combines with part of the carbon, forming a

homogeneous, crystalline mass, which is calcium carbide. It has a specific gravity of 2.2, and is only fusible at the high temperature at which it has been originally obtained. When heated in the air it burns into calcium carbonate, CaCO_3 . Water instantly reacts with it, forming calcium hydrate and acetylene, according to the equation:



8. **Calcium nitrate** is formed in nature in the vicinity of dwellings, in the soils of cellars, in damp walls, and as an efflorescence on the walls of stables and other places through which urine or other organic liquids percolate; it is, consequently, frequently called *lime saltpeter*, or *wall saltpeter*. It may be prepared by saturating nitric acid with calcium carbonate. It has the formula $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and is deliquescent and soluble in water and alcohol. When heated and exposed to sunlight, calcium nitrate becomes luminous in the dark.

9. **Calcium carbonate**, CaCO_3 , occurs widely distributed in nature as the different varieties of limestone, marble, calc-spar, and chalk. It is dimorphous, crystallizing in rhombic crystals having a specific gravity of 3, as *aragonite*, and in hexagonal rhombohedra with a specific gravity of 2.7 as in *calcite*.

Limestone and *chalk* are either amorphous or indistinctly crystalline calcium carbonate, while *marble* is a granular crystalline form. Oxides of iron and manganese are sometimes present in marble and give it a variegated appearance. When bituminous matter is present it is known as black marble.

Calcium carbonate is nearly insoluble in pure water. The presence of carbon dioxide in water increases its solubility. Heated above 500°C ., calcium carbonate decomposes into quicklime and carbon dioxide.

10. **Calcium sulphate**, CaSO_4 , occurs in nature in combination with 2 molecules of water as *gypsum*, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. It is also found in nature in the anhydrous condition as the

mineral *anhydrite*. In combination with water this compound also forms transparent prisms known as *selenite*. By heating gypsum to between 150° and 200°C . it loses water and forms *plaster of Paris*. This mixed with water combines with it and solidifies. When the gypsum is burnt it loses water and forms the hemihydrate, $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$. This is more soluble than either the anhydrous salt or the salt containing 2 molecules of water, and part dissolves in the water and forms a saturated solution. The hydrate is thus formed and, as the solution is supersaturated with respect to the hydrate, some of it crystallizes out in this form, and the water thus released dissolves more of the hemihydrate. The process is thus repeated until the whole of the hemihydrate is converted into the hydrate. Plaster of Paris mixed with glue is frequently used for ornamental purposes under the name of *stucco*.

Precipitated calcium sulphate is used in the manufacture of paper, under the name of *pearl hardener*. Calcium sulphate is used in stables and farmyards for absorbing the ammonia of the decomposing animal excrements, which would otherwise be lost to the manure. It is contained in many natural waters, and is one of the chief causes of the permanent hardness that is not removed by boiling. It is sparingly soluble in water, so that sulphates will precipitate calcium only from relatively strong solutions. The aqueous solution of CaSO_4 precipitates barium salts immediately, but strontium salts only after an interval, on account of the greater solubility of SrSO_4 . Calcium sulphate is most soluble in water having a temperature of 35°C .; 1 part of it then dissolves in 400 parts of water. It is insoluble in alcohol. Boiling HCl dissolves it, and deposits it in needle-shaped crystals on cooling. It is used also as a filler for writing papers.

11. **Chloride of lime**, or bleaching powder, has been treated under chlorine.

12. **Calcium fluoride**, CaF_2 , is found in nature as the mineral *fluorspar*. It occurs in small quantities in the bones and the enamel of the teeth, in the ashes of some plants, and in sea-water. It is insoluble in water and is only decomposed

by strong acids. When heated it becomes luminous, fuses at a red heat, hence serves as a flux in the smelting of ores.

13. Calcium sulphide, CaS , is obtained by heating calcium sulphate at a high temperature with charcoal. It is a yellowish-white mass that is luminous in the dark after having been exposed to the sunlight. This fact was first observed by Marggraf in 1750. Canton in 1768 described a method for obtaining the sulphide by strongly heating oyster shells with sulphur.

Calcium hydrosulphide, $\text{Ca}(\text{SH})_2$, is obtained when a cream of calcium hydroxide is acted on by hydrogen sulphide. It crystallizes in colorless prisms with 6 molecules of water and readily melts in its water of crystallization. Warmed in a stream of hydrogen sulphide it decomposes into calcium sulphide and hydrogen sulphide.

Calcium sulphide forms the main constituent in the tank waste of the alkali works. A solution of calcium hydrosulphide is used in tan works as a depilatory.

14. Calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, occurs in combination with calcium fluoride in the minerals *apatite* and *phosphorite*. It forms approximately 80 per cent. of the ashes of all bones. Calcium phosphate is precipitated as a white gelatinous mass when disodium phosphate is added to an ammoniacal solution of calcium chloride. It is nearly insoluble in water but is soluble in hydrochloric acid, in nitric acid, and in acetic acid.

15. Primary calcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, frequently called *acid calcium phosphate*, is prepared by the action of sulphuric acid on the normal phosphate. It is the chief constituent of the superphosphates used as fertilizers. It is prepared in the pure state by dissolving calcium phosphate in the required amount of phosphoric acid, and allowing the solution to evaporate when the salt crystallizes out in rhomboidal plates containing 1 molecule of water. It is readily soluble in water, and when heated changes to the metaphosphate $\text{Ca}(\text{PO}_3)_2$.

16. Calcium pyrophosphate, $\text{Ca}_2\text{P}_2\text{O}_7$, is formed when *secondary calcium phosphate, CaHPO_4 ,* precipitated when disodium phosphate is added to a weak acetic-acid solution of calcium chloride, is strongly ignited. The pyrophosphate, when heated to a red heat, forms a perfectly transparent glass possessing all the properties of ordinary glass.

17. Calcium silicates are found, associated with silicates of other metals, in many minerals. They also enter into the composition of most glasses. Window glass, for instance, contains the silicates of calcium and sodium, and Bohemian glass those of calcium and potassium.

STRONTIUM

Symbol Sr. Atomic weight 87.63. Valence II.

18. History and Occurrence.—Strontium was distinguished as a peculiar substance by Hope in 1792. Davy, in 1808, recognized it as an elementary body, though it was not until 1855 that Bunsen and Matthiessen obtained it in the pure state. Strontium occurs in nature both as sulphate and as carbonate. The former, known as the mineral *celestite* (so called from the blue tint of many specimens*), is mostly found in beautiful crystals associated with the native sulphur in Sicily; the latter is found in the mineral *strontianite*—derived from Strontian, Scotland, where the mineral was first observed, and from which the metal obtained its name *strontium*.

19. Preparation and Properties.—Metallic strontium is usually prepared by the electrolysis of its chloride, though it has been obtained by distilling strontium amalgam in hydrogen. The amalgam was prepared by the action of sodium amalgam on a saturated solution of strontium chloride.

Strontium is a pale-yellow metal of specific gravity 2.54; it is harder than lead, is malleable and ductile, melting at red heat, but is not volatile at a red heat. If exposed to air, it

* Said to be due to the presence of a phosphate of iron.

burns vividly with a characteristic crimson flame. Though it is quite permanent in dry air, it decomposes water readily, with the evolution of hydrogen.

COMPOUNDS OF STRONTIUM

20. Strontium oxide, or strontia, SrO , is, as a rule, obtained by igniting strontium nitrate, $Sr(NO_3)_2$. It is a grayish-white porous mass, is infusible, and unites energetically with water to form the hydroxide.

21. Strontium dioxide, or peroxide, SrO_2 , crystallizes in pearly plates containing 8 molecules of water when a solution of the oxide or hydroxide in water is treated with hydrogen peroxide. On being heated the anhydrous dioxide remains as a light white powder, which gradually loses oxygen.

22. Strontium hydroxide, $Sr(OH)_2$, is obtained as the result of the union of strontium oxide and water. It is prepared on a large scale by heating celestite with brown iron ore and coal dust. It forms colorless, deliquescent, quadratic crystals having the formula $Sr(OH)_2 \cdot 8H_2O$. It is more soluble in water than is calcium hydroxide, is used in sugar refining, and when strongly heated is converted into strontium oxide.

23. Strontium nitrate, $Sr(NO_3)_2$, is prepared in considerable quantity by dissolving strontium carbonate—usually the mineral strontianite—in nitric acid. It is largely used in pyrotechnics to produce red fire. It is soluble in water, but insoluble in alcohol.

24. Strontium chloride, $SrCl_2$, crystallizes in needles having the composition $SrCl_2 \cdot 6H_2O$, and having a bitter taste. It is deliquescent and fairly soluble in alcohol; the alcoholic solution burns with a red flame.

25. Strontium Carbonate and Sulphate.—The carbonate of strontium, *strontianite*, $SrCO_3$, and strontium sulphate, *celestite*, $SrSO_4$, are found in nature, as has been mentioned. They are insoluble in water, and are deposited

as white precipitates on adding a soluble carbonate or sulphate to the solution of a strontium salt. Strontium sulphate is, however, less soluble than calcium sulphate and more soluble than barium sulphate. Strontium salts impart a red tinge to the flame of any substances with which they are in combination.

BARIUM

Symbol Ba. Atomic weight 137.37. Valence II.

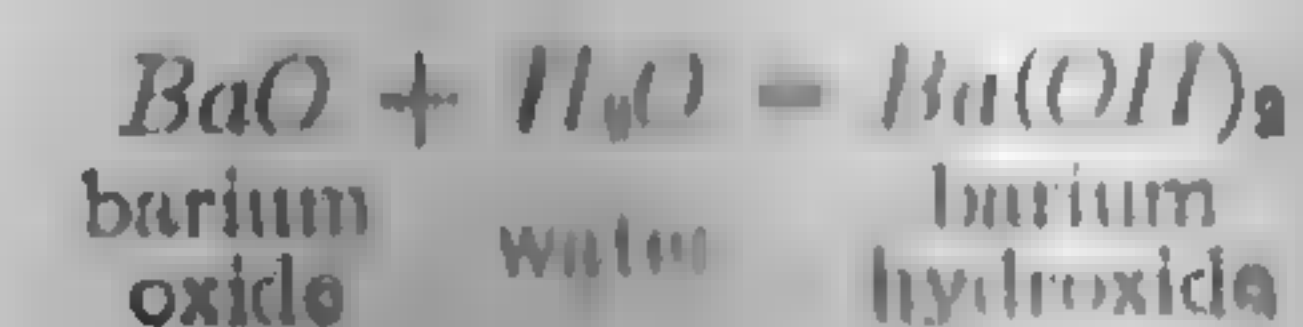
26. History and Occurrence.—Barium was first recognized as a new element by Scheele in 1774. Davy, in 1808, succeeded in isolating the metal. Its name is derived from the Greek word *barys*, meaning *heavy*, because of the high specific gravity of all the barium compounds. It occurs in nature largely as the sulphate in *heavy spar*, or *barite*, as *witherite*, or barium carbonate, and in lead and silver ores.

27. Preparation and Properties.—Metallic barium is prepared by the electrolysis of the fused chloride, or by the electrolysis of the carbonate or sulphate mixed with mercury and mercuric oxide and distilling the amalgam.

Barium is a silver-white malleable metal with a specific gravity of 3.7, melts at $850^\circ C$., and boils at $1,150^\circ C$. It is stable in dry air but oxidizes rapidly in moist air, and decomposes both water and alcohol.

COMPOUNDS OF BARIUM

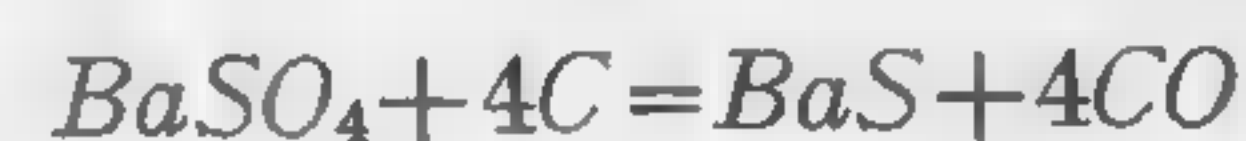
28. Barium oxide, or baryta, BaO , is obtained by heating the nitrate. It is a heavy, gray, porous solid of specific gravity 5.5; it unites energetically with water, the action being accompanied by a hissing sound and the evolution of much steam. The product of the reaction, known as *caustic baryta*, is the hydroxide $Ba(OH)_2$, which is obtained according to the equation:



Barium hydroxide is soluble in 2 parts of boiling water, and on cooling is deposited in large tabular crystals. The solution of barium hydroxide in water is known as *baryta water*. Crystallized barium hydroxide may be produced by adding 113 grams of powdered barium nitrate to 340 cubic centimeters of a boiling solution of NaOH containing 85 grams of commercial caustic soda in 567 cubic centimeters of water; the solution becomes turbid from the separation of barium carbonate produced from the sodium carbonate in the hydroxide; it is boiled for some minutes and then filtered; on partial cooling, some crystals of undecomposed barium nitrate are deposited; and, if the clear liquid is poured off into another vessel and stirred, it deposits an abundant mass of crystals of barium hydroxide, having the composition $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. These crystals soon effloresce and become opaque when exposed to the air.

29. Barium dioxide, or peroxide, BaO_2 , is obtained by passing dry oxygen over barium oxide heated to dull redness. It is a gray, sometimes greenish-looking, porous substance, and loses its second atom of oxygen when heated to bright redness.

30. Barium sulphide, BaS , is obtained by reducing barium sulphate with charcoal, according to the equation:



or by passing hydrogen sulphide over heated barium oxide until no more water is formed.

Like calcium sulphide, it is phosphorescent. When dissolved in water, it is decomposed into barium hydroxide and barium hydrosulphide.

31. Barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, is the barium compound mostly used in the laboratory; it may be obtained by saturating the solution of barium carbonate with hydrochloric acid. Barium chloride is deposited in tabular crystals, belonging to the type of the orthorhombic prisms, which are unaltered in the air and have the formula $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. It is easily

soluble in water, but insoluble in alcohol, as well as in strong acids. It is poisonous.

32. Barium chlorate, $\text{Ba}(\text{ClO}_3)_2$, is of importance because of its employment in pyrotechnics. It is prepared by adding barium chloride to a solution of sodium chlorate. On concentration the sodium chloride crystallizes out first and is separated from the solution, which is then evaporated and the chlorate purified by recrystallization. It crystallizes in shining, tabular prisms, with 1 molecule of water; it is readily soluble in water and alcohol. Mixed with sulphur and charcoal, it imparts a brilliant green color to the flame of the burning mixture.

33. Barium nitrate, $\text{Ba}(\text{NO}_3)_2$, is prepared by decomposing barium carbonate with dilute nitric acid, filtering and evaporating the solution. It crystallizes in regular octahedrons, the crystals being transparent and unaltered in the air. One part of barium nitrate requires for its solution about 20 parts of water at 12°C ., 5 parts of water at 15°C ., and 2.8 parts at 106°C . When heated to redness, barium nitrate gives off oxygen, nitrogen, and red vapors, leaving a residue of BaO . It is used in pyrotechnics and for the manufacture of an explosive powder known as saxifragine.

34. Barium sulphate, BaSO_4 , found abundantly in nature as barite, or heavy spar, has the specific gravity of 4.5. It is almost insoluble in water and acids, except in concentrated sulphuric acid, where the solution, on cooling, deposits crystals of acid barium sulphate, $\text{BaH}_2(\text{SO}_4)_2$. Artificial barium sulphate is used by painters instead of white lead, under the name of *permanent white* (*blanc fixe*), and as an adulterant of white lead. It is also employed for glazing paper, cards, etc., and is prepared by mixing the solution of a barium compound with dilute sulphuric acid, when the barium sulphate separates as a white precipitate, which is collected, washed, and dried. The prepared barium sulphate has more body, or covering power, than the finely ground mineral.

35. Barium carbonate, $BaCO_3$, occurs abundantly in nature as the mineral *witherrite*, in shining rhombic prisms. It is prepared as a dense white powder with a specific gravity of 4.3, by pouring a solution of barium chloride into an excess of a boiling solution of sodium carbonate. It is insoluble in water, and fuses at a white heat, losing carbon dioxide and forming the basic carbonate $BaO \cdot BaCO_3$.

REVIEW OF THE METALS OF THE ALKALINE EARTHS

36. Owing to their close relationship, barium, strontium, and calcium form a rather interesting natural group of metals. They exhibit a well-defined gradation in their attraction for oxygen; namely, barium is more readily tarnished or oxidized, even in dry air, than strontium, and strontium, again, more readily than calcium. The hydroxides of the metals exhibit a similar gradation in properties; barium hydroxide does not lose water, even when strongly heated, whereas the hydroxides of strontium and calcium are readily decomposed by a red heat. Barium hydroxide and strontium hydroxide are far more soluble in water than is calcium hydroxide, and they all exhibit a very decided alkaline reaction, which entitles them to the name of *alkaline earths*. Among the other compounds of these metals, the sulphates may be mentioned as presenting a gradation of a similar description; for barium sulphate may be considered insoluble in water, while strontium sulphate is slightly soluble, and calcium sulphate rather freely soluble.

GLUCINUM

Symbol Gl. Atomic weight 9.1. Valence II.

37. Occurrence.—Glucinum, also called *beryllium*, occurs in nature principally as a double silicate of glucinum and aluminum in the mineral beryl, which has the formula $Al_2Gl_2(SiO_3)_6$. It also occurs in the emerald, the composition of which is the same as beryl, but which is colored green by a little chromium, and in chrysoberyl, $Gl(AlO_2)_2$.

38. Preparation and Properties.—Glucinum is obtained by heating its chloride with metallic potassium or sodium, when the sodium or potassium unites with the chlorine and sets the glucinum free. It is a hard silver-white, ductile metal with a specific gravity of 1.85, melting below $1,000^\circ C$. It is stable in the air, does not decompose steam at a red heat, and is strongly electropositive. When heated in a finely divided condition, it burns in the air with great brilliancy. It is readily soluble in hydrochloric acid, but insoluble in nitric acid in the cold, and only slowly when warmed. Potassium hydroxide dissolves glucinum with the evolution of hydrogen.

COMPOUNDS OF GLUCINUM

39. When a soluble hydroxide is added to the solution of a glucinum salt, the hydroxide, $Gl(OH)_2$, separates as a white gelatinous precipitate that dissolves in an excess of the alkaline hydroxides with the formation of the corresponding glucinate. A large quantity of water decomposes these glucinates, and the hydroxide is again precipitated. If the hydroxide is heated, water is given off and the oxide remains. **Glucinum oxide, GlO ,** is a light, white, infusible powder that dissolves quite readily in either acids or alkalies, and is insoluble in water.

40. Glucinum chloride, $GlCl_3$, is prepared by heating a mixture of glucinum oxide with charcoal in a stream of chlorine.



It may also be obtained by acting on the element with chlorine. It is deliquescent, and dissolves readily in water with the evolution of heat. When the solution in water is evaporated it crystallizes with 4 molecules of water.

41. Glucinum sulphate is formed by dissolving glucinum oxide, or better, the hydroxide, in dilute sulphuric acid. From a solution in water it crystallizes with 4 molecules of water, $GlSO_4 \cdot 4H_2O$. The crystals are readily soluble in water, have a sweet taste, and effloresce on exposure to the air. If a solution of the sulphate is heated with glucinum hydroxide, basic glucinum sulphates are formed.

The formation of glucinates from the hydroxide, the decomposition of the chloride when evaporated, and the formation of basic sulphates show that glucinum is a weak base and possesses acid properties.

MAGNESIUM

Symbol *Mg*. Atomic weight 24.32. Valence II.

42. History and Occurrence.—Magnesium carbonate, under the name of *magnesia alba*, has been known in Europe since the beginning of the 18th century, but, although Black in 1775 showed that this substance appeared to be a peculiar earth, its composition was not known until 1808, when Davy obtained the metal. The magnesium he obtained was rather impure; and not until 1830, and then by Bussy, was it produced in an approximately pure form. Bunsen and Matthiessen, in 1852, prepared it by electrolysis of fused magnesium chloride; and, in 1857, Deville and Caron obtained it in large quantities by acting on the chloride with sodium, a process subsequently improved by Sonstadt.

Magnesium is found abundantly, like calcium, in all three natural kingdoms, as *magnesite*, $MgCO_3$; *dolomite*, $CaMg(CO_3)_2$; *Epsom salts*, $MgSO_4 \cdot 7H_2O$, etc. Among minerals containing this metal, those with which we are most familiar are certain combinations of silica and magnesia, well known by the names of *talc*, *steatite*, or *French chalk*, *asbestos*, and *meerschaum*; nearly all minerals containing magnesium possess a peculiar soapy feeling.

43. Preparation and Properties.—Magnesium may be prepared by the electrolysis of the chloride, but is more conveniently prepared by decomposing the chloride with sodium. In carrying out this process, magnesium chloride, fluorspar, and sodium are mixed and highly heated. As dry magnesium chloride is rather difficult to obtain, the double chloride of magnesium and potassium, $KMgCl_3$, is frequently substituted.

At the present time magnesium is prepared by the electrolysis of fused carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$. The carnallite is fused by external heat in a cylindrical steel vessel, which is made

the cathode terminal. The anode is a carbon rod placed in a porcelain cylinder through which a current of coal gas or hydrogen is passed to remove all the oxygen and chlorine evolved. The metal magnesium separates at the cathode and floats on the surface of the fused electrolyte.

Magnesium is a silver-white, brilliant metal having a specific gravity of 1.76. It is somewhat malleable and ductile, but is not very tenacious. It melts at $632.6^\circ C.$, boils at $1,100^\circ C.$, and may be obtained crystallized in regular octahedrons. It oxidizes readily in moist air, but is not attacked by dry air. Acids attack it with ease, and it unites directly with most negative elements, including nitrogen. It burns when heated with an intense white light. It decomposes many salts with an evolution of hydrogen.

The light produced by burning magnesium is particularly rich in chemically active rays, producing chemical changes similar to those caused by sunlight, so that photographs may be made by its means in the absence of sunlight.

COMPOUNDS OF MAGNESIUM

44. Magnesium oxide, or magnesia, MgO , occurs in nature as the mineral *periclase* crystallized in isometric forms; it is the sole product of the combustion of magnesium in the air, and is left whenever its carbonate, hydroxide, or nitrate is ignited. It forms a soft, bulky, white powder that slowly attracts moisture from the air, to form the hydroxide, $Mg(OH)_2$. Magnesia is employed in medicine and in the manufacture of refractory lining for furnaces.

45. Magnesium hydroxide, $Mg(OH)_2$, is found in nature as the mineral *brucite*. It is obtained as a white, gelatinous mass when potassium or sodium hydroxide is added to a solution of a magnesium salt. It can be dried at $100^\circ C.$ without decomposition, but is decomposed into the oxide at a low red heat. It absorbs carbon dioxide from the air, and is almost insoluble in water. It is used to a great extent in extracting sugar from sugar beets.

46. Magnesium chloride, $MgCl_2$, is most readily prepared by igniting the double chloride of magnesium and ammonium; the ammonium chloride is thereby driven off and the magnesium chloride left as a white, translucent, crystalline mass, readily fusible and somewhat volatile. It is very soluble in water, and deliquesces readily. It may be prepared also by the action of hydrochloric acid on magnesium carbonate or oxide. It occurs in spring waters, sea-water, and in various salt beds. It has a saline, bitter taste.

47. Magnesium carbonate, $MgCO_3$, occurs in nature in rhombohedra, isomorphous with calcite, as the mineral *magnesite*. It also occurs combined with calcium carbonate as *dolomite*. It is present in nearly all natural waters, causing temporary hardness, the magnesium carbonate being precipitated by boiling. It is obtained as a white voluminous powder by drying the precipitate formed when an alkali carbonate is added to a solution of a magnesium salt. It has a bitter taste and an alkaline reaction. Magnesium carbonate is soluble in water containing carbon dioxide, but on boiling, it separates out in crystals containing 3 molecules of water.

48. Magnesium sulphate, $MgSO_4$, exists in solution in sea-water, and in certain purgative mineral waters, such as those of Epsom, in England, whence the name *Epsom salt*, so frequently applied to this substance. It also occurs as *kieserite*, $MgSO_4 \cdot H_2O$. It was formerly produced by heating dolomite and then treating the residue with sulphuric acid. It is now prepared by treating the crude kieserite on sieves with water, which dissolves the magnesium and sodium chlorides. The kieserite, together with insoluble impurities, drops through the sieves and is allowed to harden in conical wooden casks and is then dried and powdered. In this state it contains from 80 to 90 per cent. of magnesium sulphate. It is then purified by crystallization.

Magnesium sulphate crystallizes in small, colorless prisms or needles, with 7 molecules of water, has a bitter, saline taste, and is soluble in water. The crystals fuse easily and lose 6 molecules of water at $150^\circ C.$; the last molecule of water,

can, however, be driven off only at a temperature of $200^\circ C.$ From its intimate relationship to the compound, this last molecule of water is termed *water of constitution*.

Magnesium sulphate forms a series of double salts with the sulphates of the alkalies, of which the double sulphate of magnesium and potassium, $MgK_2(SO_4)_2 \cdot 6H_2O$, is an example.

49. Phosphates of Magnesium.—The *normal orthophosphate*, $Mg_3(PO_4)_2$, is contained in the bones of animals and in the seeds of cereals. It is obtained as a hydrated white precipitate having the formula, $MgHPO_4 \cdot 7H_2O$, when disodium phosphate is added to the solution of magnesium salts.

Magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, is a frequent constituent of urinary calculi, and is precipitated by disodium phosphate from ammoniacal solutions of magnesium salts. The precipitation is greatly accelerated by stirring. It is sparingly soluble in water, and nearly insoluble in ammonia. When heated it loses water and ammonia, forming magnesium pyrophosphate, thus:



FAMILY 2, GROUP B

INTRODUCTION

50. Family 2, Group B, consists of the metals *zinc*, *cadmium*, and *mercury*. The relationship between zinc and cadmium is much closer than between these metals and mercury; they resemble magnesium quite closely, while in some ways mercury resembles the members of Family 1, Group B. Like magnesium, zinc and cadmium are bivalent, and form but one series of salts. Mercury, on the other hand, forms one series, known as *mercurous salts*, in which its valence appears to be 1, and another, known as *mercuric salts*, in which its valence is 2. Just as glucinum, the first member of Group A of this family, is a weak base, and shows acidic tendencies, so also

zinc, the first member of Group B, is a rather weak base, and exhibits acid tendencies, while the other members of the family do not. The hydroxides of glucinum and zinc dissolve in alkaline hydroxides, forming glucinates and zincates, while the hydroxides of the other members of this family are insoluble in alkaline hydroxides.

ZINC

Symbol Zn. Atomic weight 65.37. Valence II.

51. History and Occurrence.—Zinc occupies a high position among useful metals, being peculiarly fitted, on account of its lightness, etc., for the construction of pipes, roofs, etc. An ore of zinc was used by the ancient Greeks, under the name *cadmia*, in the manufacture of brass. In Europe, zinc was first discovered in the 18th century, it having been, until that time, imported from China. The name *zinc* was given to the metal by Paracelsus in the 16th century.

The ores of zinc are found pretty abundantly in this country, in England, Transylvania, Hungary, and Silesia.

Metallic zinc, as a rule, does not occur free in nature, though it is claimed to have been found in the native state near Melbourne, Australia. Its chief ores are *smithsonite*, or *zinc carbonate*, $ZnCO_3$, *blende*, or *zinc sulphide*, ZnS , *zincite*, or *red zinc ore*, in which zinc oxide, ZnO , is associated with the oxides of iron and manganese, and *franklinite*, which appears to be a mixture of the oxides of iron and zinc. Zinc carbonate is one of the most important ores of zinc. It is found largely in England, and a basic carbonate, $Zn_3(OH)_2CO_3$, occurs in Spain. Formerly the name *calamine* was given to both the carbonate and silicate, but at present the carbonate is known as *smithsonite*; the hydrated silicate, $Zn_2SiO_4 \cdot H_2O$, as *calamine*; and the anhydrous silicate, Zn_2SiO_4 , as *willemite*.

52. Preparation.—Zinc is extracted from its ores by first roasting them in a reverberatory furnace, and then distilling them, mixed with charcoal, or powdered anthracite coal, in closed iron or earthen vessels. By the action of the carbon

of the charcoal or coal, the oxygen is removed from the zinc oxide that constitutes the roasted ore, and the zinc thus set free, being volatile, distils over into suitable receivers. The process, as a whole, varies in different countries; in Silesia, Germany, this distillation is effected in peculiarly shaped muffles of fireclay, in Belgium in earthenware tubes, and in England in fireclay retorts.

An English zinc furnace is shown in Fig. 3. It is conical in shape, and has an interior dome, within which six crucibles are placed, each of them having a hole in the bottom, through which an iron pipe passes to take away the zinc vapor. The crucibles are charged with the mixture of roasted zinc ore and coke, the covers are cemented on, and the crucibles are gradually raised to bright redness. At first the carbon monoxide burns at the mouth of the tube, but soon the greenish flame of zinc appears; the tube is then lengthened, and the condensed zinc is collected in suitable vessels placed beneath. It is afterwards remelted, cast into ingots, and sent out under the commercial name *spelter*. The spelter, or zinc of commerce, is impure, containing as a rule



FIG. 3

small quantities, or only traces—according to the constitution of the ore—of iron, copper, lead, cadmium, carbon, and arsenic. It may be purified to a certain degree by repeated meltings with small quantities of niter, but the last traces of impurity can be removed only by fractional distillation in *vacuo*.

In the Belgian process, which is the one most generally used at present, the ore, from which all sulphur has been removed by roasting, is mixed with from one-third to one-half its weight of powdered anthracite coal and placed in retorts. These retorts are tube-shaped, made of fireclay, and are from 3 to

5 feet in length and from 6 to 10 inches in diameter. After being charged, a conical clay tube 18 inches long is luted to the open end of the retort, and to this adapter is fitted a condenser of sheet iron, which catches any metal and also condenses the zinc fumes. The retorts are placed usually four deep in a large furnace holding from forty to sixty retorts, and fired by either coal, oil, or gas.

53. Properties.—Zinc is a bluish-white, highly crystalline metal; its specific gravity is about 7; its fracture is laminated and brilliant. It is hard and brittle at ordinary temperatures, and also at 200° C., but between 100° C. and 150° C. it is malleable and ductile and may be rolled into thin sheets. At 419° C. it melts, and at 918° C. it boils, evolving a vapor having half the normal density, from which the conclusion is drawn that its molecule is monatomic. When heated to redness in air, it volatilizes and burns with a greenish flame into a smoke of oxide that falls in bulky, white flakes, which were formerly known as *flowers of zinc*, or *philosopher's wool*.

Zinc dissolves with the evolution of hydrogen in hydrochloric and sulphuric acid, and in solutions of potassium and sodium hydroxides. When perfectly pure, it is dissolved with difficulty by dilute sulphuric acid at ordinary temperatures, and the easy solubility of the commercial metal must be attributed to the presence of small quantities of foreign metals. The latter, being electronegative in contact with zinc, form voltaic couples, in which the zinc is the more oxidizable metal.

The great strength of iron has been ingeniously combined with the durability of zinc in the so-called *galvanized iron*. This is manufactured by coating clean iron sheets with melted zinc, thus affording a protection much needed in and around large towns, where the oxides of sulphur arising from the combustion of coal, and the acid emanations from various factories, greatly accelerate the corrosion of unprotected iron. The iron plates thus coated are at first thoroughly cleaned and then dipped into a vessel of melted zinc, the surface of which is coated with sal ammoniac (ammonium chloride), in order to dissolve the zinc oxide that forms on the surface of the metal

and might adhere to the iron plate so as to prevent its becoming uniformly coated with the zinc.* A more firmly adhering coat of zinc is obtained by first depositing a thin film of tin on the surface of the iron plate by galvanic action, whence the name *galvanized iron* is derived.

COMPOUNDS OF ZINC

54. Zinc oxide, ZnO , occurs in nature as *red zinc ore*, or *zincite*. It is the sole product of the combustion of zinc in the air, and is also prepared by heating the carbonate or nitrate. It is used under the name of *zinc white* as a stable white paint, and is also used in medicine. It is prepared for medicinal purposes by igniting the basic carbonate which is precipitated by treating a solution of zinc sulphate with sodium carbonate. It is an amorphous white powder, becoming a lemon yellow when hot, has a specific gravity of 5.6, absorbs carbon dioxide from the air, is insoluble in water but soluble in dilute acids, ammonium hydroxide, and ammonium carbonate. Heated in the oxyhydrogen flame, it emits a brilliant white light. When used as a paint it has the advantage over white lead of being uninjurious to the health of the users, and is not affected by hydrogen sulphide. It has the tendency, however, of being more liable to crack and peel off than the white lead paint.

55. Zinc hydroxide, $Zn(OH)_2$, is obtained as a gelatinous precipitate when caustic alkalis are added to solutions containing zinc, thus:



The precipitate dissolves in an excess of alkali, and, if this be not too great, is reprecipitated by boiling. Zinc hydroxide is readily decomposed by heat, thus:



*The sal ammoniac acts on the heated zinc according to the equation $Zn + 2NH_4Cl = ZnCl_2 + 2NH_3 + H_2$, and the zinc chloride that is formed dissolves the oxide from the surface of the metal, producing zinc oxychloride.

56. Zinc sulphide, ZnS , is found crystallized in nature, forming the mineral *sphalerite*, or *blende*. It is generally yellowish brown in color, has a resinous luster, and is translucent. It is precipitated from zinc solutions by alkali sulphides as a white precipitate, easily soluble in acids. The natural sulphide is easily converted into the sulphate by roasting it with free access of air.

57. Zinc chloride, $ZnCl_2$, is prepared in the laboratory by dissolving zinc in hydrochloric acid, or by acting on the metal with chlorine. If zinc is dissolved in hydrochloric acid and the solution is concentrated by evaporation, crystals having the composition $ZnCl_2 \cdot H_2O$ are deposited. If these are heated to expel the water, or if the original solution is evaporated to dryness, the chloride is partly decomposed with the formation of basic chloride, hydroxide, and oxide of zinc. The anhydrous chloride has a strong affinity for water and is sometimes used as a desiccating agent; it is a white, granular powder, of specific gravity 2.9, melts a little over $100^\circ C.$, and is soluble in water and alcohol. It is used on a large scale for the weighting of cotton goods. A solution having a specific gravity of 1.7 and containing an excess of the oxide will dissolve silk.

58. Zinc sulphate, $ZnSO_4$, crystallizes from an aqueous solution with 7 molecules of water as $ZnSO_4 \cdot 7H_2O$. The crystals are rhombic prisms. As with magnesium sulphate, 6 of these molecules of water are quite easily expelled by heat, while the seventh is only driven off with difficulty. This last molecule is known as water of constitution, and it has been suggested

that the formula of the salt is probably $\begin{array}{c} H-O \\ H-O \end{array} \rangle S \begin{array}{c} O \\ O \\ O \end{array} \rangle Zn$.

Zinc sulphate is prepared also by dissolving zinc in sulphuric acid, and on a large scale by the careful roasting of blende at a low red heat. It is known as *white vitriol*, is colorless, has an astringent, metallic taste, effloresces in dry air, and is somewhat soluble in water. It is frequently used in pharmacy, and for dyeing purposes.

CADMIUM

Symbol Cd. Atomic weight 112.4. Valence II.

59. History and Preparation.—Cadmium was discovered in 1817 by Hermann, and also by Strohmeyer, the latter giving to it the name *cadmium*, from *cadmia*, the ancient name of *zinc ore*; it is generally found associated with zinc, and also as the sulphide in the mineral *greenockite*. It occurs as an impurity in commercial zinc, but, as it is more volatile than zinc, it comes over in the first products of its distillation; these are dissolved in acid, and the cadmium precipitated by zinc, in the metallic state.

60. Properties.—Cadmium resembles zinc, its compounds being analogous to those of this metal, but it is whiter, heavier, and more easily volatile and fusible than this metal. It is ductile and malleable at ordinary temperatures, but becomes brittle at about $82^\circ C.$, and if bent when in this condition it crackles like tin. It has a specific gravity of 8.7, melts at $320^\circ C.$, and crystallizes in regular octahedrons on cooling. It is not attacked by air, but acids act on it slowly. At a red heat it burns, producing brown fumes of oxide. Cadmium is used in the preparation of alloys of low melting point.

COMPOUNDS OF CADMIUM

61. Cadmium oxide, CdO , may be obtained by calcining either cadmium carbonate or nitrate. Its color varies from yellowish brown to dark brown. It is reduced at high temperatures by carbon and by hydrogen, its reduction taking place more readily than that of zinc oxide.

62. Cadmium sulphide, CdS , occurs in nature as greenockite in the form of bright-yellow, hexagonal prisms, terminated by six-sided pyramids. It is prepared in the laboratory by precipitating a solution of cadmium salt with hydrogen sulphide or a soluble sulphide, an amorphous precipitate of a fine yellow color being thus obtained.

63. Cadmium iodide, CdI_2 , is obtained by digesting finely divided cadmium with iodine in the presence of water. It crystallizes from its aqueous solution in transparent, hexagonal prisms having a brilliant luster. It is soluble in water and alcohol, melts at $350^\circ C.$, and gives off iodine when heated to a higher temperature. Cadmium iodide, as well as cadmium bromide, $CdBr \cdot 4H_2O$, is used in photography.

64. Cadmium sulphate, $CdSO_4$, is obtained by dissolving either the metal, its oxide, or its carbonate in dilute sulphuric acid. It crystallizes with 8 molecules of water, $CdSO_4 \cdot 8H_2O$.

65. Cadmium chloride, $CdCl_2$, crystallizes from solution of the metal or oxide in hydrochloric acid in rectangular prisms having 2 molecules of water. These readily effloresce in the air, lose water on heating, melt at $590^\circ C.$, and sublime at a higher temperature.

66. Cadmium differs from all other metals in forming a yellow sulphide insoluble in alkalis, so that its salts, mixed with excess of ammonia and treated with H_2S , give a yellow precipitate.

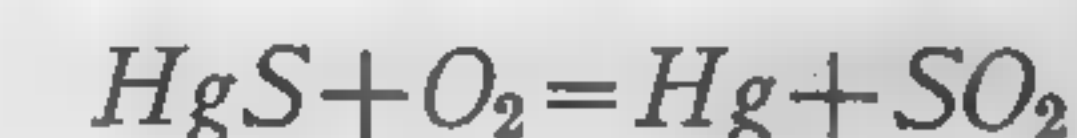
MERCURY

Symbol Hg. Atomic weight 200.6. Valence I and II.

67. History and Occurrence.—Mercury has been known from the earliest times; its Latin name *argentum vivum*, of which the English name *quicksilver* is a literal translation, refers to its fluidity as well as to its color. The name mercury, from the planet of that name, was given by the alchemist to all volatile substances, but only this one has retained it. The symbol of mercury, *Hg*, is derived from the Latin name *hydrargyrum*. It occurs native only sparingly, the chief ore being the sulphide, called *cinnabar*, which is found principally in Idria, Austria; Almaden, Spain; and New Almaden, California.

68. Preparation.—The process of extracting the mercury from its ore is a rather simple and easy one. It usually

consists in roasting the ore in a reverberatory furnace, or even in a small blast furnace, with access of air, by which the sulphur is oxidized to sulphur dioxide, and the mercury set free and volatilized, according to the equation:



Sometimes lime or oxide of iron is mixed with the ore, and the sulphur retained in this way as sulphide of calcium or iron, depending on which has been used. The condensation of the vapors of mercury is, however, a matter of some difficulty, and the methods employed vary considerably in different localities.

At Idria, the vapors are passed through chambers and a series of twin tubes of cast iron cooled externally by water. They are so arranged that the condensed metal collects and runs down into the receptacle at the base of each tube. In Almaden, twelve parallel series of conical clay receivers, called *aludels*, luted together, are interposed between the furnace and its flue; each of these is about 20 inches long, and a series extends about 20 yards. The lines of aludels are of sufficient length to allow the vapors and gases to cool nearly to the temperature of the air, and so arranged as to allow the condensed mercury to gravitate toward a common channel where it collects.

69. Properties.—Mercury is a brilliant, silver-white metal. It has a specific gravity of 13.50 at 0° and is the only metal that is liquid at the ordinary temperatures. Cooled to -39.5° , it solidifies to a malleable, tin-white mass, easily sectile, and crystallizing in regular octahedrons. Even at ordinary temperatures mercury has a small vapor tension, and gives off minute quantities of its vapor into the atmosphere in contact with it. It boils at $357^\circ C.$, yielding a colorless vapor of specific gravity 0.070. When heated almost to its boiling point in air, it becomes coated with the red oxide, HgO . It is unaltered in air; neither hydrochloric nor dilute sulphuric acid attacks it, but boiling, strong sulphuric acid, and even dilute nitric acid, dissolve it readily. Chlorine and sulphur unite directly with it.

Mercury is used in the arts for filling thermometers and barometers, and very extensively for extracting gold and silver from their ores. With most of the metals it forms alloys, known as *amalgams*; in some cases these amalgams possess a definite composition and crystalline form, for example, Hg_6Na is brittle and crystallizes in regular forms. Sodium amalgam is a convenient reducing agent, for when brought into contact with water or solutions in water, hydrogen is evolved. Tin amalgam is sometimes used for producing the silver coating on glass for mirrors.

Mercury forms two series of compounds, the mercurous, in which this metal is monovalent, and the mercuric, in which it is divalent. It will be seen that the two series differ very considerably in properties.

COMPOUNDS OF MERCURY

70. Mercurous oxide, Hg_2O , is a dark-brown or black powder obtained by digesting mercurous chloride, $HgCl$, with potassium hydroxide. It is very unstable, and is decomposed by the action of light or heat into mercuric oxide and metallic mercury.

71. Mercuric oxide, HgO , may be prepared by either a dry or wet method. The first consists in decomposing mercuric nitrate by heat; the salt is gradually heated in a flask in a sand bath until vapors cease to be disengaged. The oxide thus prepared is an orange-red, granular, and crystalline powder. It may also be prepared by heating mercury in air for some time. By the wet method, mercuric oxide is prepared by decomposing a solution of a mercuric salt by potassium hydroxide, a yellow precipitate of mercuric oxide being thus obtained.

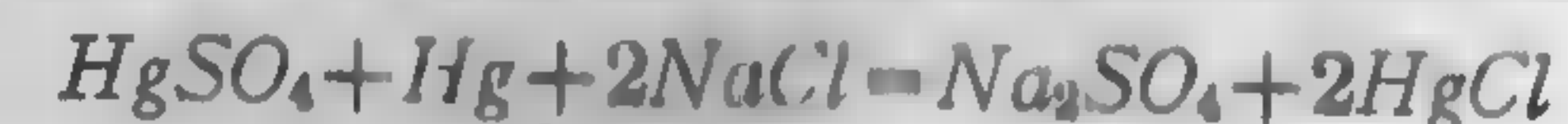
When mercuric oxide is heated, it assumes a dark-red color and decomposes, if the temperature is above $400^\circ C.$, into oxygen and mercury. Mercuric oxide is soluble in acids, yielding mercuric salts. Hydroxides of mercury are unknown.

72. Mercuric sulphide, HgS , occurs in nature as the mineral cinnabar, both massive and in red rhombohedral

crystals. It is obtained artificially by direct synthesis. The combination takes place when the elements are triturated in the cold, in the proportion of 100 parts of mercury and 18 parts of sulphur. A black mass is thus obtained that is sublimed in iron vessels. The black sulphide may be obtained also by treating a mercuric salt with H_2S . It becomes red when sublimed.

The pigment *vermilion* is a finely divided mercuric sulphide having a beautifully rich scarlet color. It is prepared by triturating for several hours, in a mortar, 300 parts of mercury and 114 parts of flowers of sulphur, and adding to the black sulphide thus obtained 75 parts of potassium hydroxide and 400 parts of water. The mixture is maintained at a temperature of about $45^\circ C.$, being continually triturated with a pestle. As soon as the powder has acquired a fine scarlet color, it is rapidly washed with hot water and dried. It is employed in painting, coloring sealing wax, and for various other purposes. It is now thought that mercurous sulphide does not exist, but that the precipitate formed when a mercurous salt is treated with hydrogen sulphide is a mixture of mercuric sulphide and mercury.

73. Mercurous chloride, $HgCl$, ordinarily called *calomel*, is precipitated whenever a chloride is added to a solution of a mercurous salt. It occurs in nature in tetragonal prisms in the mineral horn quicksilver. Commercially, it is prepared by subliming a mixture of mercuric sulphate, mercury, and salt:



The heavy yellowish-white powder that condenses is washed with water to remove any mercuric chloride. It is not soluble in water, though chlorine water and nitric acid dissolve it by converting it into mercuric chloride. It sublimes between 400° and $500^\circ C.$ without melting. Calomel is gradually decomposed by light, and is blackened by ammonium hydroxide.

74. Mercuric chloride, $HgCl_2$, also known as *bichloride of mercury*, and as *corrosive sublimate*, is obtained by heating mercury in chlorine. It is manufactured by heating dry mercuric sulphate with an equal quantity of dry salt. A small

amount of manganese dioxide is usually added to the mixture to prevent the formation of calomel. The mixture is placed in large glass vessels and heated, when the corrosive sublimate is converted into a vapor and condenses on the cooler part of the vessel in a white, transparent, or lustrous crystalline mass. It has an acrid, persistent, metallic taste, melts at 265°C ., and sublimes at 300°C ., and is somewhat soluble in water and in alcohol. It is used for the preservation of anatomical specimens, for dressing furs and skins, and as an antiseptic in surgery.

Mercuric chloride is a violent poison. Its antidote is the white of an egg, this forming an insoluble compound with the poison, thus rendering it inert to the stomach. Mercuric chloride unites with a number of other chlorides, forming readily soluble double salts. It also unites with mercuric oxide, forming oxychlorides.

75. Mercurous iodide, HgI , is, as a rule, prepared by direct synthesis, 100 parts of mercury and 63.5 parts of iodine being triturated until the whole is converted into a green powder, which is then washed with boiling alcohol and dried. It may also be obtained by precipitating a mercurous salt with potassium iodide. Mercurous iodide is a rather unstable compound, being decomposed by light as well as by heat, the latter decomposing it into mercury and mercuric iodide. The same decomposition is affected by potassium iodide and the alkaline chlorides.

76. Mercuric iodide, HgI_2 , is prepared by pouring a solution of 100 parts of potassium iodide into a solution of 80 parts of corrosive sublimate, HgCl_2 . A scarlet-red precipitate of mercuric iodide is thrown down. It is absolutely necessary that the compounds be mixed in exactly the proportions given; an excess of potassium iodide would dissolve the mercuric iodide first precipitated.

Mercuric iodide is nearly insoluble in water; it is slightly soluble in boiling alcohol, which deposits it, on cooling, in small, red, octahedral crystals.

On heating to 254°C ., mercuric iodide melts to a dark-yellow liquid that solidifies, when cooled, to a yellow mass. At a

higher temperature the liquid boils and its vapor condenses in a dark-yellow liquid that solidifies to a yellow mass; at the same time, right rhombic prisms of a yellow color sublime. If these are rubbed with a glass rod or other hard substance, they instantly become red, first at the point of contact, then throughout the entire mass.

Mercuric iodide forms a compound with potassium iodide that is soluble in water. A solution of this potassium mercuric iodide is not precipitated by potassium hydrate, but the liquid rendered alkaline by the latter compound is a very sensitive test for ammonia (Nessler's test), with which it gives a precipitate or a brown cloud more or less intense, according to the quantity of ammonia present.

77. Mercuric cyanide, $\text{Hg}(\text{CN})_2$, is of importance as being the salt that, on heating, yields cyanogen gas (an organic compound). It is prepared by boiling mercuric sulphate and potassium ferrocyanide together in aqueous solution, or by dissolving mercuric oxide in hydrocyanic acid. It crystallizes in white needles and is soluble in about 8 parts of cold water.

78. Sulphates of Mercury.—A *mercurous sulphate*, Hg_2SO_4 , and a *mercuric sulphate*, HgSO_4 , are obtained by heating together mercury and sulphuric acid, the particular one formed depending on whether an excess of mercury or sulphuric acid, respectively, is used. The mercuric sulphate is the more important salt. It consists of white crystals that, on heating, undergo decomposition with the formation of mercurous sulphate. In presence of water the salt is very liable to become basic.

79. Nitrates of Mercury.—*Mercurous nitrate*, HgNO_3 , and *mercuric nitrate*, $\text{Hg}(\text{NO}_3)_2$, are formed from mercury and nitric acid under similar conditions to the sulphates, and, like them, form basic salts in the presence of water. For the weaker acids the affinity of mercury is too feeble to admit the formation of stable salts; the phosphates, carbonates, borates, and silicates have either not been prepared at all, or are obtained as basic compounds of variable composition.

FAMILY 3, GROUP A

CHEMICAL RELATIONS

80. Family 3, Group A, consists of the elements *boron*, *aluminum*, *scandium*, *yttrium*, *lanthanum*, *ytterbium*, and probably some other rare elements. While there is a general resemblance between the different members of this group, there is a gradation in properties from the lighter to the heavier.

As has been seen in Family 5, Group B, the lighter members, nitrogen and phosphorus, are decidedly acidic or non-metallic in character, while the heaviest member of the group, bismuth, is basic or metallic. The same thing is noticeable in this group. Boron, the lightest member of the group, is almost devoid of basic properties, and must be classed as a non-metal; aluminum—the second member—has both acid and basic properties, but as both are weak and the basic properties appear to predominate, it is usually considered as a metal. The other members have higher atomic weights and are more strongly basic.

There are some points of resemblance between this group and Family 5, Group B, and as that group is acidic in character, boron is sometimes treated there. It undoubtedly belongs to Family 3, Group A, however, and will be treated at this point.

BORON

Symbol B. Atomic weight 11.0. Valence III.

81. **History and Occurrence.**—Boron occurs almost exclusively in the mineral kingdom, but it is claimed that it has been found in grape vines and in a few other plants. Under the Arabic name *buraq* (corrupted into borax), a salt obtained from certain lakes in Thibet, which contains boron as an essential constituent, has been imported into Europe for a long

time, and has been used in medicine, in working metals, and in imitating precious stones.

From this borax, in 1702, Homberg obtained boron trioxide, from which Davy, in 1807, by utilizing electricity, and Gay-Lussac and Thenard, in 1808, by chemical processes, obtained pure boron. Wöhler and Deville succeeded, in 1856, in crystallizing it. The mineral *sassolite* is *boric acid*, H_3BO_3 ; and *borax*, *boracite*, and *ulexite* are natural borates of sodium, magnesium, and calcium, respectively.

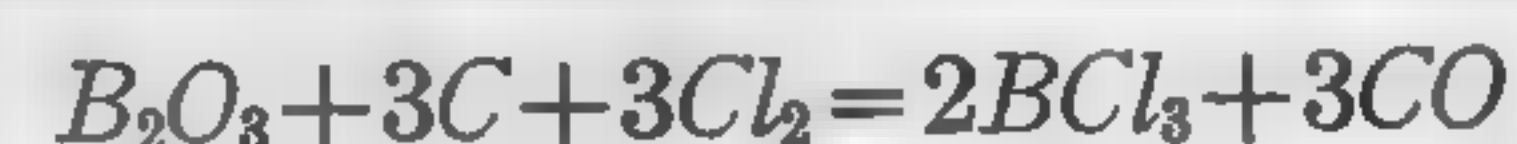
82. **Preparation and Properties.**—Boron possesses two distinct forms—amorphous and crystalline. Amorphous boron is obtained by heating boron trioxide with potassium. The boron thus obtained is a greenish-brown powder, of specific gravity 2.45, that burns with a green flame at $700^\circ C.$, and is a rather poor conductor of electricity. It is readily oxidized by nitric acid and is infusible at the heat of the oxyhydrogen flame.

The crystalline variety is obtained either by dissolving the amorphous modification in melted aluminum, when boron crystallizes out upon the aluminum cooling, or by melting boron trioxide and aluminum together and subsequently treating the mixture with hydrochloric acid to remove the impurities such as aluminum and carbon, from the crucible. Boron crystallizes in short yellow or brownish-yellow quadratic octahedrons with a specific gravity of 2.65. The luster and hardness of boron crystals is next to that of the diamond, and they will scratch both corundum and the ruby. The crystalline modification of boron is infusible and is insoluble in any acid. Aqua regia attacks it slowly. It is slowly soluble in melted caustic soda or potash.

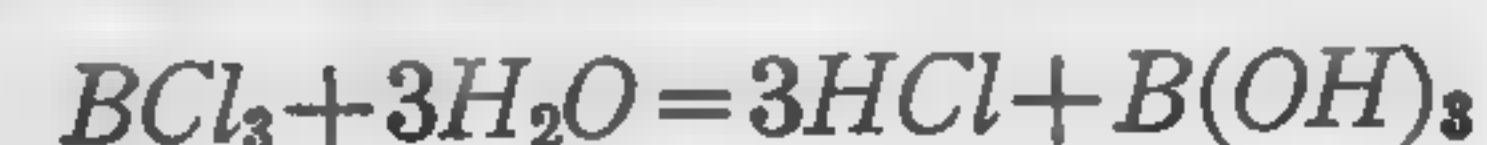
Heated to $410^\circ C.$ in chlorine boron forms boron trichloride. Heated to redness, boron absorbs nitrogen, forming a white, infusible, insoluble powder of boron nitride, *BN*.

HALOGEN COMPOUNDS OF BORON

83. Boron trichloride, BCl_3 , may be obtained by heating crude amorphous boron in a current of chlorine, or by passing dry chlorine over a strongly heated mixture of boron trioxide and charcoal, according to the equation:

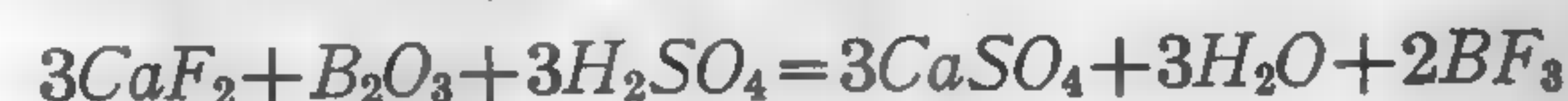


In a pure state, boron trichloride is a colorless, highly refractive liquid of specific gravity 1.35 at 17° C., boils at 18.2° C., and fumes in the air. It is readily decomposed by water into boric and hydrochloric acids:



84. Boron tribromide, BBr_3 , is obtained either by direct combination of its constituents or by passing bromine vapor over a heated mixture of charcoal and boron trioxide. It is a strongly fuming, colorless liquid, specific gravity 2.69, that boils at about 90° C. Its vapor is colorless, and it is decomposed by water the same as the trichloride.

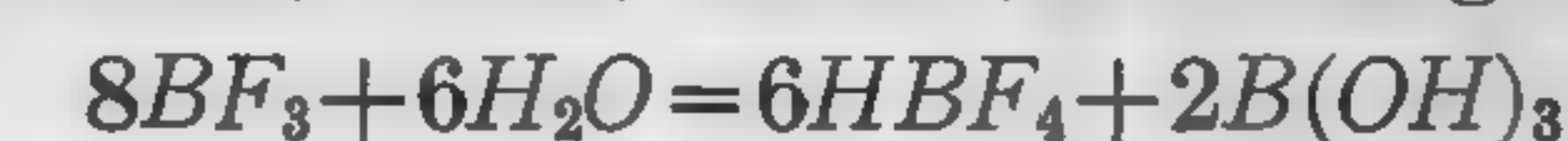
85. Boron trifluoride, BF_3 , was discovered by Gay-Lussac and Thenard in 1810. It is prepared by heating an intimate mixture of 1 part of boric oxide and 2 parts of finely powdered calcium fluoride with 12 parts of sulphuric acid; the gas evolved is collected over mercury. The occurring reaction may be expressed by the equation:



Boron trifluoride is a colorless gas having an extremely suffocating odor; it fumes in the air and condenses to a liquid at -101° C.; it is decomposed by water, and must, therefore, be collected over mercury. Its affinity for water is so great that it carbonizes paper and certain organic substances in the same way as does strong sulphuric acid. Potassium and sodium burn brilliantly when heated in it.

The solution of boron fluoride in water is accompanied by a chemical reaction that is shown when the aqueous solution

of this gas, saturated at ordinary temperatures, is cooled to 0° C., for crystals of boric acid are deposited, and a very acid liquid, *fluoboric acid*, HBF_4 , formed, according to the equation:



BORON AND OXYGEN

86. Boron trioxide, B_2O_3 , is formed whenever boron burns in air or oxygen. It is usually obtained by igniting its hydroxide, boric acid, $B(OH)_3$. A viscid mass is left, which solidifies to a colorless, transparent, and brittle glass having a specific gravity of 1.83. It unites readily with water, volatilizes at a white heat, and dissolves nearly all metallic oxides at a red heat.

87. Boric acid, $B(OH)_3$, or H_3BO_3 , was discovered by Homberg in 1702. It occurs free in nature in volcanic districts, as in Tuscany, where it issues, mixed with steam and gaseous matter, from fissures in the earth into natural or artificial little lakes or ponds, known as *lagoons*, or *lagoni*. The gases (*suffioni*) contain sensible traces of boric acid, which is dissolved by the water of the lagoni, which soon becomes charged with the acid; on evaporation this water furnishes the crude boric acid. Boric acid may be prepared from sodium borate or borax by dissolving 3 parts of it in 12 of boiling water, adding 1 part of sulphuric acid, and allowing the whole to cool. The boric acid separates out in white, crystalline scales of specific gravity 1.48 that are somewhat greasy to the touch. They are soluble in 30 parts of water at 18° C., and freely soluble in alcohol, the latter solution burning with a greenish flame. The aqueous solution of boric acid is feebly acid; it changes blue litmus solution to a wine color and turns turmeric paper brown. This constitutes the *normal* or *orthoboric* acid. When heated to 120° C., it loses 1 molecule of water and is converted into *metaboric acid*, HBO_2 . If the latter is maintained for some time at a temperature of 140° C., it is converted into *tetraboric acid*, $H_2B_4O_7$, according to the equation:



Boric acid shows a strong tendency to condensation, thus forming multiple salts. *Borax*, or *sodium tetraborate*, $\text{Na}_2\text{B}_4\text{O}_7$, is an example. Borax occurs naturally in the waters of certain lakes in Thibet and in the waters of Borax Lake and Lake Clear, about 250 miles north of San Francisco, California. It is used largely as a flux in working metals.

ALUMINUM

Symbol Al. Atomic weight 27.1. Valence III.

88. History and Occurrence.—Aluminum is one of the most abundant and, at the same time, most widely distributed constituents of the earth's crust. It derives its name from the word *alumen*, meaning alum. For a long time *alumina*, or *aluminum oxide*, was confounded with lime, from which it was first distinguished by Marggraff in 1754. In 1826 Oersted first prepared the chloride, and Wöhler, in 1828, obtained the metal from this salt. This process was made a commercial one by St. Claire Deville in 1854. Aluminum does not occur free in nature. It is found, as nearly pure aluminum oxide, in *corundum*, *ruby*, and *sapphire*; in *diaspore*, AlOOH ; in *bauxite*, $\text{Al}_2\text{O}(\text{OH})_4$; in *feldspar*, $\text{K}_2\text{Al}_2\text{SiO}_6$; in *cryolite*, Na_3AlF_6 ; and as a silicate in all clays and in many minerals.

89. Preparation.—Aluminum was first produced commercially by the process invented by St. Claire Deville, which consists in reducing the chloride with sodium. By an improvement in this method sodium aluminum chloride, cryolite, and sodium are mixed together and heated in a furnace. A violent action takes place, great heat is evolved, and the liquefied mass of slag and metal gathers in the furnace. The latter is drawn off and cast into ingots. Tissier, at Amfreville, France, makes aluminum from the mineral cryolite, after a method proposed by H. Rose; and in the United States it is now produced in considerable quantities from the same mineral by electrolysis, a process devised by Hall.

The Hall electrolytic method for the preparation of aluminum has almost entirely superseded the other method mentioned.

In this method pure anhydrous aluminum oxide is dissolved in a bath of fused cryolite and fluorspar in an iron pot lined with carbon which forms the cathode. The anode is composed of one or more carbon rods. The bath is kept at a temperature of about $1,000^\circ \text{C}$. By this process the aluminum oxide is reduced, the metallic aluminum falling to the bottom of the pot, while the oxygen unites with the carbon of the anode. The fluoride remains unchanged; hence, by frequently withdrawing the metal and renewing the aluminum oxide, the process is made continuous.

90. Properties and Uses.—Aluminum is a white metal with a somewhat bluish luster when polished. It crystallizes in octahedrons, and is a good conductor of heat and electricity. It is ductile, malleable, highly sonorous, and very light, its specific gravity being 2.5 to 2.7. It is less fusible than tin and zinc, but more so than silver, its fusing point being nearly 654°C . It requires a very high temperature to vaporize it. Like zinc, it is most easily rolled and bent between 100° and 150°C .

Aluminum is unaltered by the air, even by moist air. When heated in thin sheets in a current of oxygen, it burns and is converted into aluminum oxide. Nitric and sulphuric acid scarcely attack it. Hydrochloric acid dissolves it readily, disengaging hydrogen; it is also immediately attacked by boiling solutions of potassium or sodium hydrates, the hydrogen being disengaged and alkaline aluminates formed.

The remarkable lightness of this metal renders it extremely useful in the manufacture of beams of chemical balances, and of small weights, such as the decigram, centigram, and milligram, since these weights when made of aluminum are more than three times larger than those of brass, and nearly nine times larger than when made of platinum; besides, the relative indestructibility of aluminum by the fumes of acids makes these weights still more valuable. The metal has also been lately used in the manufacture of cooking utensils, and especially of canteen vessels for military purposes, where, on account of its lightness and ability to resist vegetable acids, it has proved itself extremely useful. Aluminum, in the form of powder,

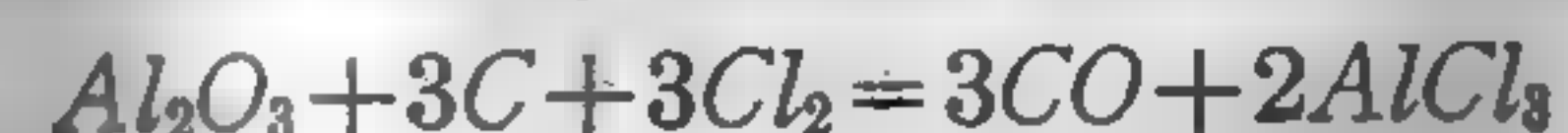
is a powerful reducing agent, the combination with oxygen being accompanied by an enormous elevation of temperature. It can be used for reducing from their oxides metals—such as chromium and tungsten—that it is difficult to reduce by other means. The great heat produced by burning aluminum powder is used for welding iron and steel. Probably the most important applications of metallic aluminum are as a conductor of the electric current and in the preparation of various alloys. The chief impurities of the commercial aluminum are traces of iron and silicon.

COMPOUNDS OF ALUMINUM

91. Aluminum oxide, Al_2O_3 , generally known as *alumina*, occurs in nature in the mineral *corundum*, which includes the precious stones known as the *ruby* and the *sapphire*, as well as the valuable polishing material called *emery*, distinguished by its extreme hardness, in which it ranks next to the diamond. It may be prepared by the combustion of the metal in oxygen or by igniting the hydrate. Fusion with potassium bisulphate or with caustic potash renders it soluble in acids.

92. Aluminum hydroxide, $Al(OH)_3$, occurs in nature as *hydrargillite*, or *gibbsite*, or as *diaspore*, $AlOOH$. These two modifications are crystalline. It is prepared by adding ammonium hydrate to the solution of a salt of aluminum, when a gelatinous precipitate separates. This is nearly insoluble in an excess of ammonium hydrate, but is readily soluble in potassium and sodium hydroxides. When washed and dried, the gelatinous hydrate shrinks very much, and forms a mass resembling gum. It is used to form insoluble, colored compounds termed *lakes*. This property is used to good advantage in calico printing, in which the compounds of aluminum are largely used as *mordants*.

93. Aluminum chloride, $AlCl_3$, sometimes written Al_2Cl_6 , is prepared by passing over an incandescent mixture of alumina and charcoal a current of chlorine, aluminum chloride and carbon monoxide being formed according to the equation:



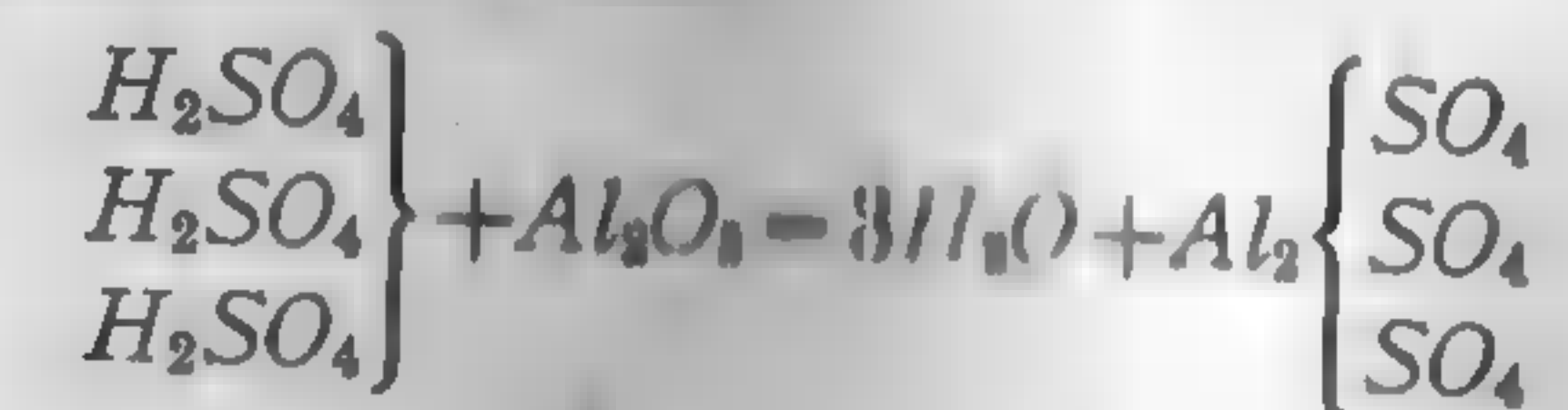
The aluminum chloride thus obtained is a white, semi-crystalline, waxy substance, having sometimes a light-yellow color; it is fusible, and volatilizes in the air at a temperature slightly above $100^\circ C$. When exposed to the air, aluminum chloride gives off white fumes and readily attracts moisture. It dissolves in water with the production of heat. A solution of aluminum chloride may be obtained by dissolving gelatinous alumina in hydrochloric acid. When this solution is evaporated, it decomposes as soon as it attains a certain degree of concentration, disengaging hydrochloric acid and leaving aluminum oxide. Aluminum chloride readily combines with sodium chloride, forming a double chloride, $NaAlCl_4$.

Authorities differ as to the molecular weight of aluminum chloride, but recent experiments make it appear that at high temperatures or when taking part in chemical reactions the formula is $AlCl_3$, while at lower temperatures it is Al_2Cl_6 .

94. Aluminum sulphate, $Al_2(SO_4)_3$, is obtained by dissolving aluminum hydrate in dilute sulphuric acid. It crystallizes with difficulty in needles and in thin pearly scales, in which state it contains 18 molecules of water of crystallization; it dissolves in 2 parts of cold water, and has a sweet, astringent taste. When slowly heated, it first loses its water of crystallization until at a higher temperature it gives off sulphur trioxide, leaving a residue of alumina, according to the equation:



Aluminum sulphate represents 3 molecules of sulphuric acid, in which the 6 atoms of hydrogen have been replaced by 2 atoms of aluminum, thus:

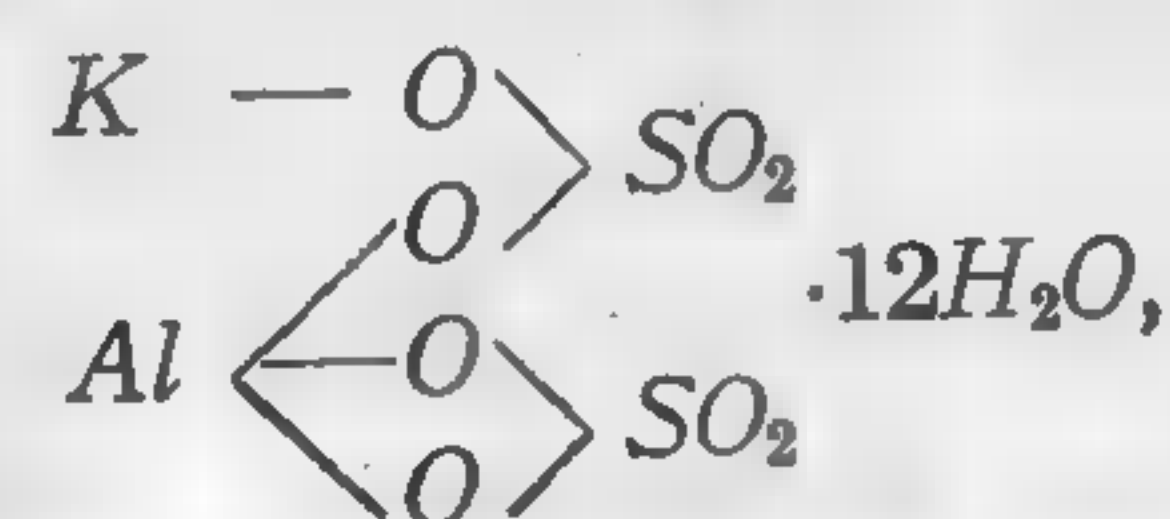


It is used as a mordant in dyeing, for the treatment of sewage, and for weighting of paper.

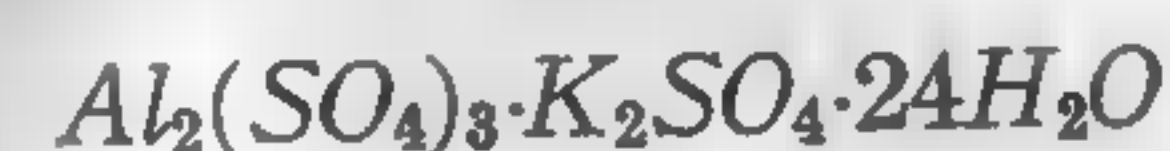
95. Aluminum and potassium double sulphate, more generally known as *alum*, $AlK(SO_4)_2 \cdot 12H_2O$, is obtained

as a crystalline deposit by adding to a concentrated solution of potassium sulphate a concentrated solution of aluminum sulphate, and stirring the mixture well with a glass rod. It is only sparingly soluble in cold water, but dissolves more easily in hot, and quite abundantly in boiling water, being deposited from the latter, on cooling, in voluminous, transparent octahedrons, and has a specific gravity of 1.7. When heated, these crystals melt in their own water of crystallization; in losing this water the melted mass swells considerably.

Alum may also be obtained crystallized in cubes. It is prepared in this form near Civita Vecchia, Italy, by working a mineral that contains the elements of alum with a large excess of alumina; this mineral is known as *aluminite*, and the cubical alum is known as *Roman alum*. This cubical variety may be prepared in the laboratory by adding a small quantity of potassium carbonate to a hot solution of ordinary alum, so that the precipitate first formed will be redissolved on agitating the liquid; on cooling, cubical, opaque crystals are deposited. These are formed under the influence of a small quantity of basic sulphate (aluminum sulphate combined with an excess of alumina) contained in the liquid, and which probably enters into the constitution of the crystals. With this slight difference, octahedral and cubical alum represents the same composition. The graphic formula of alum is probably



but the ordinary formula is sometimes written



96. **Ammonium alum** is obtained by adding ammonium sulphate to solution of aluminum sulphate. It possesses a composition analogous to that of ordinary alum, with which it is isomorphous. Its formula is $AlNH_4(SO_4)_2 \cdot 12H_2O$. It is very often substituted in the arts for potassium alum, being cheaper than the latter. When strongly calcined, it leaves a residue of pure alumina.

Other alums are known, in which iron, manganese, and chromium play the part taken by aluminum in ordinary alum; these are all isomorphous. By the action of sulphuric acid on the sesquioxides of the above metals, sulphates are formed analogous to aluminum sulphate, and of which the composition is expressed by the general formula $X_2(SO_4)_3$. With the sulphates M_2SO_4 they form alums, all of which crystallize in regular octahedrons, and which can be mixed in one and the same crystals without the form of the latter being affected by the mixture. The most important of these compounds are: *Manganese alum*, $MnK(SO_4)_2 \cdot 12H_2O$; *iron alum*, $FeK(SO_4)_2 \cdot 12H_2O$; *chrome alum*, $CrK(SO_4)_2 \cdot 12H_2O$. It is seen that each of these presents an atomic composition similar to that of ordinary alum.

97. Mineral Silicates of Aluminum.—The silicates of aluminum occur in combination with silicates of other elements in large quantities in the crust of the earth. Aluminum is very frequently replaced by iron in the form of Fe_2O_3 , thus rendering the chemical formulas of these minerals rather complicated. The chief silicates of aluminum are: *Topaz*, $Al_2SiO_4F_2$; *garnet*, $(Mg.Fe)_3Al_2Si_3O_{12}$; *orthoclase*, $Al(Si_3O_8)K$; *kaolin*, $H_2Al_2Si_2O_8 \cdot H_2O$; and *albite*, $NaAl(Si_3O_8)$.

SCANDIUM

98. Scandium, *Sc*, atomic weight 44.1, valence III, was discovered in 1880. It is found in the rare minerals gadolinite and euxenite. Its compounds resemble those of aluminum. Its oxide, known as *scandia*, has the formula Sc_2O_3 ; the metal itself has not been isolated. It is infusible and insoluble in alkalis. Like aluminum, scandium forms a sulphate $Sc_2(SO_4)_3$, a double sulphate $KSc(SO_4)_2$, and other salts resembling those of aluminum. The salts of scandium are all colorless and show no absorption bands. It is somewhat more basic than aluminum, however.

YTTRIUM

99. Yttrium, *Y* or *Yt*, atomic weight 89, valence III, is, like scandium, found in gadolinite and euxenite. It is also found in samarskite, a North Carolina mineral, and in some other rare minerals. Its hydroxide, $Y(OH)_3$, is obtained by treating a solution of one of its salts with potassium hydroxide. The hydroxide thus formed is not dissolved by an excess of the potassium hydroxide. Yttrium hydroxide is more basic than aluminum hydroxide. It unites with the carbon dioxide of the air to form a carbonate. The oxide, Y_2O_3 , is obtained by heating the hydroxide or nitrate. The chloride is easily obtained and crystallizes with 6 molecules of water, $YCl_3 \cdot 6H_2O$.

LANTHANUM

100. Lanthanum, *La*, atomic weight 139, valence III, also occurs in gadolinite, but is more abundant in cerite, a mineral of the same type and also containing the metal cerium. It is prepared almost exclusively from cerite by treatment with nitric acid, treatment with sodium hypochlorite, and fractional crystallization. It is a white, malleable metal with a specific gravity of 6.16, and melts at $810^\circ C$. Heated in the air, it forms the oxide, La_2O_3 , and nitride, LaN . The oxide has a specific gravity of 6.5, and combines with water with the evolution of heat, forming the hydroxide, $La(OH)_3$.

YTTERBIUM

101. Ytterbium, *Yb*, atomic weight 172.0, valence III, is found in gadolinite and euxenite. Its compounds have the same form as those of aluminum, and resemble those of yttrium in properties. Its hydroxide, $Yb(OH)_3$, is insoluble in alkaline hydroxides, and unites with carbon dioxide. It forms an oxide, Yb_2O_3 , and other compounds which are colorless.

OTHER ELEMENTS IN FAMILY 3, GROUP A

102. Gadolinium, *Gd*, atomic weight 157.3, and samarium, *Sm*, atomic weight 150.4, are found in the minerals samarskite, gadolinite, cerite, and some others. They appear to form compounds like those of aluminum, and are generally classed in this group. The oxide of gadolinium, Gd_2O_3 , is white and the salts are colorless. Metallic samarium has a white color, melts between $1,300^\circ$ and $1,400^\circ C$., has a specific gravity of 7.7, and tarnishes readily. It forms light-yellow salts and acts as a trivalent element, although a chloride having the formula $SmCl_2$ has been prepared. This chloride forms a reddish-brown mass soluble in water. The chloride, $SmCl_3$, crystallizes in large yellow tablets having 6 molecules of water.

103. Helium, *He*, atomic weight 3.99, is obtained from the air by fractional distillation. In the liquefaction of air the portion having the lowest boiling point escapes. This gas, principally helium and neon, is compressed in a vessel and liquefied by cooling with liquid air, when the helium is separated by fractional distillation. Some rare minerals, especially cleveite, when treated with acid, give off a gas which has been shown to be helium. It is very light and appears to be incapable of chemical action. At present its place in the periodic system is not firmly established and very little is known in regard to its relation to other elements. Helium boils at $-268.5^\circ C$., its critical pressure is about 3 atmospheres, and its critical temperature about 5° absolute temperature ($-268^\circ C$.).

104. Other elements whose position in the periodic system is not definitely known, and which are obtained from the rare earths are: Holmium, *Ho*, atomic weight 163.5; erbium, *Er*, atomic weight 167.7; and thulium, *Tm*, atomic weight 168.5. All these are obtained from the same source as yttrium. All form some salts that show absorption bands, but very little is known regarding these elements.

FAMILY 3, GROUP B

105. Family 3, Group B, is composed of the three rare elements, *gallium*, *indium*, and *thallium*. Gallium is trivalent in most of its compounds, but also forms compounds in which it is bivalent. The principal compounds of indium are those in which the element is trivalent, but it also forms bivalent compounds. Thallium acts as trivalent and univalent in its compounds.

GALLIUM

Symbol Ga. Atomic weight 69.9. Valence II and III.

106. History, Occurrence, and Preparation.—Gallium was discovered in 1875 by Lecoq de Boisbaudran in a zinc blende from the mine of Pierrefitte in the valley of Argeles, Pyrenees, in France; its name is derived from *Gallia*, the Latin name of France. It is prepared by treating the ore with acids and the solution is decomposed by means of zinc. The precipitate is treated with hydrochloric acid and a precipitate again thrown down by means of metallic zinc. The solution is then saturated with hydrogen sulphide, the precipitate filtered off, and the excess of hydrogen sulphide removed from the solution by boiling. The solution is neutralized with sodium carbonate and made slightly acid with sulphuric acid, diluted and boiled when the basic sulphate of gallium is precipitated. This precipitate is dissolved in sulphuric acid, the solution is mixed with acid ammonium acetate, again saturated with hydrogen sulphide, and filtered. The filtrate is diluted with water, heated to boiling and filtered. This precipitate is dissolved in the required amount of sulphuric acid, is neutralized with potassium hydroxide and a slight excess added, and then electrolyzed, the gallium being deposited on the cathode, from which it is easily removed by bending the cathode under cold water.

107. Properties.—Gallium is a tough, grayish-white metal that can be cut with a knife. It melts at 30.1°C. , and has a specific gravity of 5.9. When melted it has the color of silver and remains liquid for a long time, even when cooled to 0°C. Heated in the air, it is only slightly oxidized, is not volatile at a red heat, and is soluble in acids and alkalies.

108. Compounds of Gallium.—*Gallium hydroxide*, $\text{Ga}(\text{OH})_3$, is precipitated as a white flocculent substance by the action of the alkali hydroxides. It is readily soluble in excess of the precipitant, but difficultly soluble in ammonia.

The *oxide*, Ga_2O_3 , is obtained by igniting the nitrate. If this is heated in hydrogen, part of it is volatilized, and the rest appears to be converted into GaO . By treating gallium with chlorine the two chlorides GaCl_2 and GaCl_3 are formed. The chlorides are both decomposed by the action of water, forming basic chlorides, and finally *gallous chloride*, GaCl_2 , is completely decomposed with the formation of the oxide.

Gallic sulphate is crystalline and deliquescent. Boiling water converts it into a basic salt. With ammonium sulphate it forms an *alum*, $\text{GaNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, that is analogous to ammonium alum.

INDIUM

Symbol In. Atomic weight 114.8. Valence II and III.

109. Indium was discovered by Reich and Richter in 1863 in a specimen of zinc blende from Freiberg, Saxony, by means of the spectrum. It is prepared by dissolving the Freiberg zinc in either hydrochloric or sulphuric acid, care being taken to leave an excess of zinc. When the action has ceased the mass is digested, when the indium is obtained as a precipitate with other metals. This precipitate is dissolved in nitric acid, the lead separated as the sulphate, and the indium and iron precipitated with ammonium hydroxide. This precipitate is dissolved in hydrochloric acid, and boiled for some time with sodium bisulphite, thus precipitating indium sulphite. This is converted into the sulphate by

boiling with nitric and sulphuric acids, and the metal precipitated with zinc.

It is a white, malleable metal, resembling lead, and dissolves readily in hydrochloric and sulphuric acids. Its specific gravity is 7.11. Its fusing point is 176°C ., and it burns with a violet light and a brown smoke, producing the oxide. It is, at ordinary temperatures, unaltered in the air, and produces a gray streak on paper. It does not tarnish in the air or in boiling water.

110. Compounds of Indium.—*Indium hydroxide*, $\text{In}(\text{OH})_3$, results, as a gelatinous precipitate, when an indium solution is treated with sodium or potassium hydroxide. It is soluble in an excess of the reagent. When the hydroxide is heated, the **oxide**, In_2O_3 , results.

The *chloride*, InCl_3 , results from the action of chlorine on the metal. The **sulphate**, $\text{In}_2(\text{SO}_4)_3$, is formed by dissolving the metal in sulphuric acid; it combines with ammonium sulphate to form the **alum**, $\text{InNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Though the term alum is usually applied to one substance, the term in its broadest sense means a double sulphate of a monad and triad, with 12 molecules of water of crystallization.

THALLIUM

Symbol Tl. Atomic weight 204. Valence I and III.

111. Thallium was discovered in the flue dust of a sulphuric-acid works in the Harz Mountains, by means of the spectroscope. It imparts a bright-green color to a flame, and obtained its name from a Greek word meaning a green branch. It may be obtained in the metallic state by adding zinc to a solution of the sulphate. It is a bluish-white metal resembling lead. It is oxidized when heated in air, and is somewhat malleable, but not ductile. Its specific gravity is about 11.8, and its fusing point about 294°C . It decomposes water at a red heat, is readily soluble in nitric and sulphuric acids, but less soluble in hydrochloric acid. It forms two classes of salts.

112. Compounds of Thallium.—*Thallous hydroxide*, TlOH , is obtained by the action of air and water on the metal, or by treating the solution of the sulphate with barium hydroxide. It dissolves readily in water, and forms an alkaline solution.

Thallic hydroxide, $\text{Tl}(\text{OH})_3$, is formed by adding potassium hydroxide to a thallic solution. When dried, this loses water, and $\text{TlO} \cdot \text{OH}$ remains.

Thallous oxide, Tl_2O , is formed by heating thallous hydroxide in such a way that oxidation is avoided. It is a black powder, melting at 300°C .

Thallic oxide, Tl_2O_3 , is obtained by burning the metal in oxygen.

Thallous chloride, TlCl , is formed by treating the metal with chlorine, or it may be obtained as a white curdy precipitate by adding hydrochloric acid to a thallous solution. This precipitate turns violet when exposed to light. By suspending thallous chloride in water, and passing a current of chlorine through it, **thallic chloride**, TlCl_3 , is formed.

Thallous sulphate, Tl_2SO_4 , is formed by the action of sulphuric acid on the metal. It unites with the sulphates of the triads forming **alums**; as, for example, $\text{AlTl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Thallic sulphate, $\text{Tl}_2(\text{SO}_4)_3$, unites with sulphates of the alkalies, forming double salts, but these do not crystallize like the alums.

In general it may be said that in the thallous condition thallium acts like the alkalies, and in the thallic condition it acts like aluminum.

INORGANIC CHEMISTRY

(PART 10)

FAMILY 4, GROUP B

GENERAL REMARKS

1. Family 4, Group B, consists of the elements *germanium*, *tin*, and *lead*. Germanium is very rare and was but recently discovered, while tin and lead have been used in considerable quantities for a long time. These elements resemble the members of Group A of the same family in some respects, but are more basic, and act principally as base-forming elements. Germanium and tin are more acidic than lead, but the basic properties predominate in all, and all are considered as metals. Each forms two series of salts, in one of which they are bivalent and in the other quadrivalent.

GERMANIUM

Symbol Ge. Atomic weight 72.6. Valence II and IV.

2. In 1886 Winkler discovered in the mineral *argyrodite*, which is a rare silver ore found near Freiberg, in Saxony, the element *germanium*. It is prepared by the reduction of the dioxide with hydrogen, carbon, or magnesium. It is a grayish-white, lustrous, crystalline metal, with a melting point of 900° C. and a specific gravity of 5.47. It combines directly with chlorine, oxygen, and sulphur when heated with them, is

stable in the air, and volatilizes at about $1,400^{\circ}\text{C}$. It forms two oxides, the lower oxide, GeO , of a dark color, the hydroxide of which is obtained by precipitating the dichloride, GeCl_2 , with potassium hydroxide; and the higher oxide, GeO_2 , by heating the metal in oxygen or with nitric acid. Its sulphides correspond with the oxides, having the formulas GeS and GeS_2 , respectively. The latter forms sulphosalts by solution in alkaline hydrosulphides.

Germanium tetrachloride, GeCl_4 , is the most stable and most important of the compounds of germanium and chlorine; it is obtained by the direct action of chlorine on the metal. It is a colorless, fuming liquid, and boils at 86°C .

The **dichloride**, GeCl_2 , is formed by heating the metal in hydrochloric-acid gas; it is a powerful bleaching and reducing agent, and by the action of water it yields an **oxychloride**, GeOCl_2 .

TIN

Symbol *Sn*. Atomic weight 119.0. Valence II and IV.

3. History and Occurrence.—Tin has been known for many thousands of years; it is spoken of by Moses (Numbers, xxxi, 22), and Homer mentions it in his Iliad. Much of the brass of the ancients was an alloy of copper and tin; as the latter was obtained from Cornwall, England, Herodotus speaks of the British Isles as the *tin islands*. The principal ore of tin is stannic oxide, known as the mineral *cassiterite*, or *tinstone*; it occurs in veins running through rocks, and also in the beds of streams, from the disintegration of these rocks. It is found principally in Cornwall, England, and Banca and Malacca, and also, though less abundantly, in New Hampshire and in California.

4. Preparation.—In the process adopted at the Cornish plants the tinstone is stamped to crush it and is then freed from gangue by washing. The tinstone, being extremely hard, is not reduced to so fine a powder as the other minerals mixed with it, and the high specific gravity of the stannic

oxide, which is 6.5, as against that of sand or quartz, which is 2.7, makes the separation by water easy and complete. After being washed, the ore is roasted in a revolving or reverberatory furnace to drive off any arsenic or sulphur that may remain in the ore. The ore is again washed after the roasting to remove the ferric oxide. The purified tin oxide, which contains between 60 and 70 per cent. of tin, is intimately mixed with about one-fifth of its weight of anthracite coal, and a small quantity of lime or fluorspar, to form a fusible slag with the silicious impurities, and reduced in a reverberatory furnace. The impure tin obtained is cast into molds and refined by the process known as *liquation*.

The furnace used for the smelting of the tin ore is shown in Fig. 1. The mixture of tin ore and coal, after being moistened to prevent the finely divided ore from being blown out of the chimney by the draft, is spread on the hearth A. The temperature of the furnace is gradually raised during the first 5 or 6 hours, the charge being stirred repeatedly. When the reduction is complete, at the end of about 6 hours, the mass is again stirred and the reduced metal allowed to run off into the iron pan B.

The slags drawn off from the furnace are carefully sorted, those containing much tin oxide being recharged with the next batch of ore, while those containing globules of metallic tin are crushed, so that the metal may be separated by washing.

5. The impure tin obtained is purified by placing the ingots in a reverberatory furnace and gradually raising the temperature to the fusing point of tin. The pure tin, being more easily fusible, melts and flows into a cast-iron basin, while

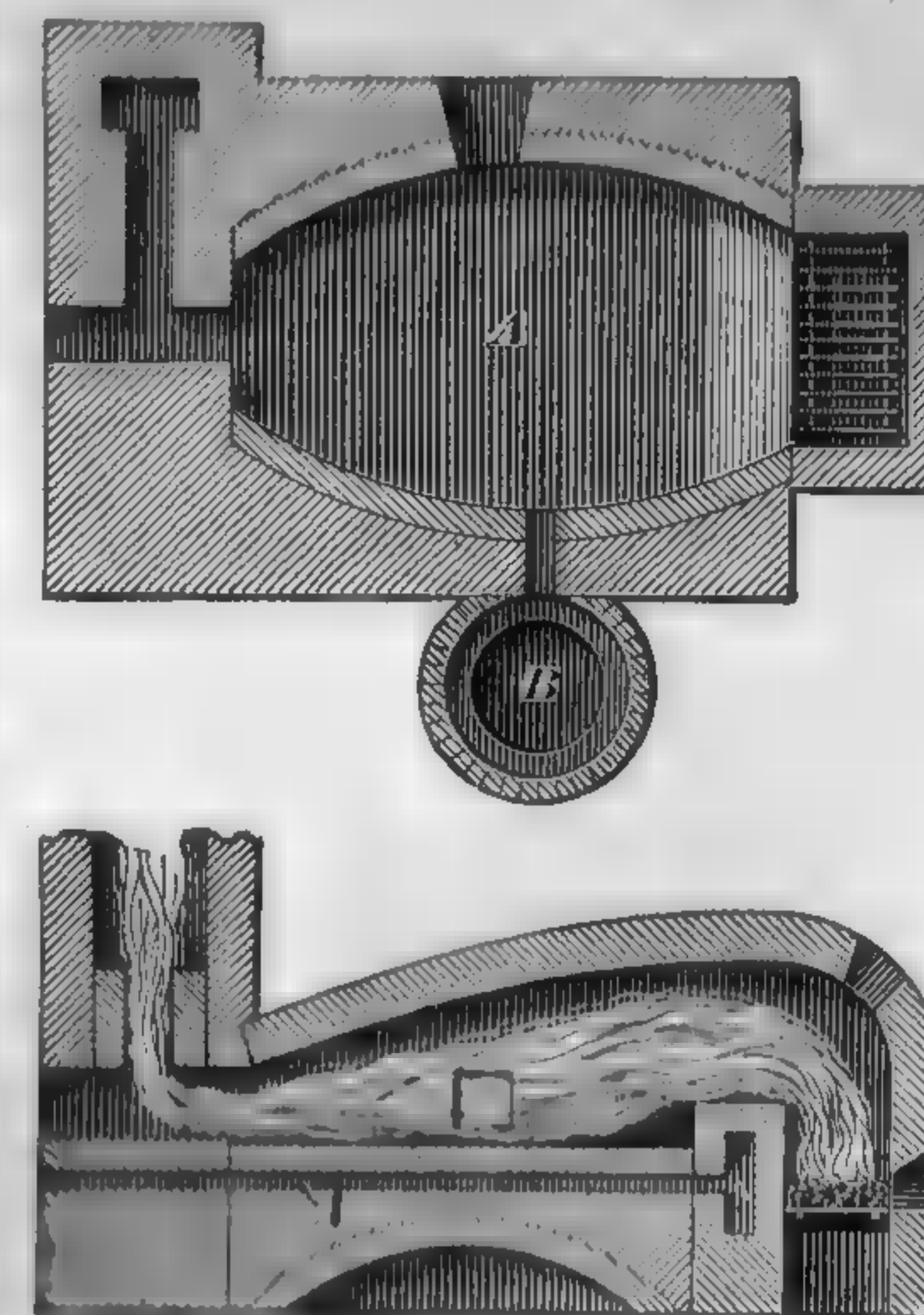


FIG. 1

the less fusible portion, an alloy of tin, iron, arsenic, and usually copper, remains as dross on the hearth of the furnace. The metal in the cast-iron basin is kept in a molten condition, and is stirred, or *poled*, with a pole of green wood. This operation may last from one to several hours, depending on the grade of tin desired. The dross separating during this operation and the residue, or *hardhead*, remaining on the hearth are afterwards recharged into the smelting furnace.

The purified tin is ladled into ingots and is known commercially as *block tin*. *Grain tin* is prepared by heating block tin until the metal becomes crystalline when, owing to its brittle nature, it is broken up with hammers or allowed to fall from a height.

The purest of commercial tins is that imported from Banca, known as *Banca tin* or *Straits tin*. Next in purity is the English tin.

6. Properties.—Tin is a brilliant-white metal that does not tarnish in the air, and has a specific gravity of 7.29. It is dimorphous, crystallizing in forms belonging to the quadratic and isometric systems. It is quite malleable and may be beaten into very thin leaves; at 100° C. it is ductile and can be drawn into wire. Its tenacity is small. It crackles when a bar of it is bent, producing that peculiar noise known as the "cry of tin." It possesses a peculiar odor, and is a good conductor of heat and electricity. Its melting point is about 232° C., and it distils at a white heat. Heated in air, it burns readily to oxide, though it retains its luster in air at ordinary temperature. It is readily attacked by acids, and dissolves in aqueous solutions of the alkalies.

7. Uses.—Tin is largely used in the arts for making tin-foil, for plating iron in the manufacture of tin plate, and also as a constituent of many important and valuable alloys. With copper it forms gun metal, speculum metal, bell metal, and bronze; with lead it forms solder and pewter. Britannia metal is an alloy of tin, antimony, and copper; and with mercury, tin yields an amalgam that is used for producing the bright reflecting surface on glass mirrors.

COMPOUNDS OF TIN

8. Stannic chloride, SnCl_4 , known to the alchemists in the middle ages as *liquor fumans Libavii*, may be obtained by the direct action of chlorine gas on tin. It is a colorless, fuming, caustic liquid that boils at 114° C. It readily unites with water, evolving heat, and forming several crystalline hydrates. With alkali chlorides it forms definite compounds, the potassium salt being K_2SnCl_6 . It is used in dyeing.

9. Stannous chloride, SnCl_2 , is prepared by dissolving tin in hydrochloric acid. If the solution is made strong enough, some of the salt will crystallize out with 2 molecules of water, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. This salt is largely used in dyeing, and is known in commerce as *tin salt*. Stannous-chloride crystals dissolve readily in water. If there is but little water present the solution is perfectly clear, but if much water is added the solution becomes turbid, owing to the formation of the basic chloride, $\text{Sn} \begin{smallmatrix} \text{OH} \\ \text{Cl} \end{smallmatrix}$. The atmospheric oxygen dissolved in water also takes part in this decomposition of stannous chloride, from which it removes part of the metal, a corresponding quantity of stannic chloride being formed.

Stannous chloride reduces many oxygenized and chlorinated compounds, and is largely used in the laboratory. It decomposes the salts of silver and mercury, setting free the metal. It instantly decolorizes the purple solution of potassium permanganate.

10. Stannic oxide, SnO_2 , is found in nature as the mineral *cassiterite*, or *tinstone*, in the form of beautiful, hard, transparent crystals of a yellowish-brown color. It may be prepared by burning the metal in air or by lighting either of the hydrates. It is obtained as a white powder, of specific gravity 6.6, that is insoluble in all acids except hydrofluoric. Owing to its hardness, it is used for polishing glass under the name of *putty powder*. When fused with alkali hydrates, it forms *stannates*.

11. Stannic Acids.—When a solution of stannous chloride in water is boiled, or a solution of a stannate is treated with

just enough acid to decompose it, a white precipitate having the composition H_2SnO_3 is formed; this is known as **stannic acid**. It dissolves readily in acids and in alkali hydrates.

When metallic tin is treated with nitric acid, a white powder is obtained that also has the composition H_2SnO_3 , but is insoluble in acids and differs in physical and chemical properties widely from the stannic acid; the name **metastannic acid** is given to this modification.

12. Stannous oxide, SnO , is of little practical importance. It is obtained by heating stannous oxalate in a closed vessel, and is a black, crystalline powder that is combustible in air. If water is added to SnO , a hydrate is formed that gradually absorbs oxygen from the air, and passes into stannic acid. With sulphuric acid it forms stannous sulphate, $SnSO_4$.

13. Sulphides of Tin.—*Stannous sulphide, SnS ,* is obtained by leading hydrogen sulphide through a stannous solution. It is a dark-brown or black precipitate that dissolves in polysulphides of the alkalis with the formation of alkali sulphostannates.

Stannic sulphide, SnS_2 , may be obtained either in the amorphous or crystalline form. By leading hydrogen sulphide through a solution of stannic chloride, stannic sulphide is obtained as a yellow amorphous precipitate. By heating a mixture of tin filings, sulphur, and ammonium chloride, or better, tin amalgam, sulphur, and dry ammonium chloride, stannic sulphide is obtained as a golden-yellow crystalline powder, known as *mosaic gold*. In this form it is used as a pigment, especially for bronzing.

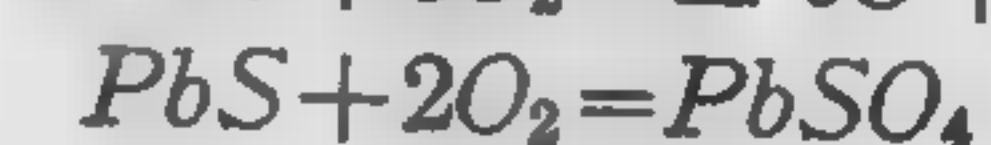
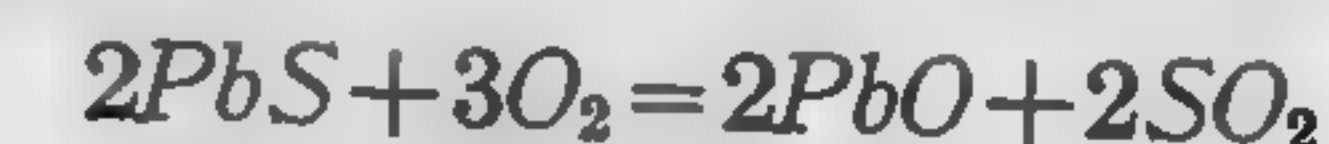
LEAD

Symbol Pb. Atomic weight 207.1. Valence II and IV.

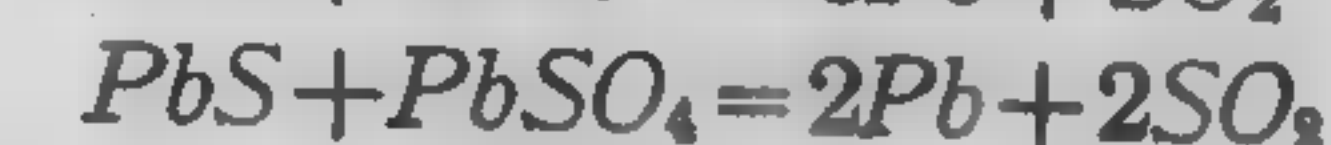
14. History and Occurrence.—Lead is one of those metals that have been known from the earliest ages of history, it is frequently mentioned in the Old Testament and other sacred writings. The Romans worked the lead ores of Spain

and of England, and the Carthaginians those of Spain, the extent of their mining and smelting operations exciting surprise, even at the present day. The principal workable ore of lead is its sulphide, *galenite*, or more popularly known as *galena*, though it occurs also somewhat abundantly as *carbonate*, or *cerussite*; as *sulphate*, or *anglesite*; as *chloroarsenate*, or *mimetite*; as *chlorophosphate*, or *pyromorphite*; and in sundry other forms.

15. Preparation.—As the preparation of lead is a comparatively simple metallurgical process, only the methods employed in its extraction from galena, which may be considered as the chief source of this metal, will be treated. For the richer ores the first part of the process is carried on in a reverberatory furnace at a moderate temperature, whereby part of the galena is converted into oxide and sulphate:



The temperature is then raised and the remaining sulphide reacts by double decomposition with the oxide and sulphate formed in the first stage:



With the exception of about 10 per cent., which remains in the slags, the lead is thus obtained in the metallic condition. After running off the lead, the residue in the slags is extracted by adding lime and a little coal, and submitting the mixture to further heating. The poorer ores are usually treated in a small blast furnace or cupola; this method may be employed for the working of slags. In this case iron or ferrous silicate is the active agent in the removal of sulphur, and the lead obtained contains considerable quantities of silver, copper, antimony, and other metals. Such a process is in use in Germany, at Clausthal and Freiberg, and in the United States.

16. For working the richer ores, a reverberatory furnace, Fig. 2, is employed. The essential elements in the construction of such a furnace are: The hopper *A*, at which the charge is introduced; the fireplace *B*, at one end and separated from the

hearth by a rather high fire-bridge; the hearth *C*, formed by molding slag in the form shown, the depression serving for collection of the molten lead, and the slopes of the hearth for spreading the charge so as to expose it to the action of the fire-gases and for working the slags; the doors *D* for regulating the supply of air and working the charge.

The first part of the process is carried out at dull red heat, and is essentially one of calcination and oxidation, during which the first two reactions take place. The doors are then closed and the temperature raised to a full red heat, when the last two reactions are effected.

17. Another form of furnace, known as the *Scotch hearth*, largely used in the northern parts of England, differs essentially

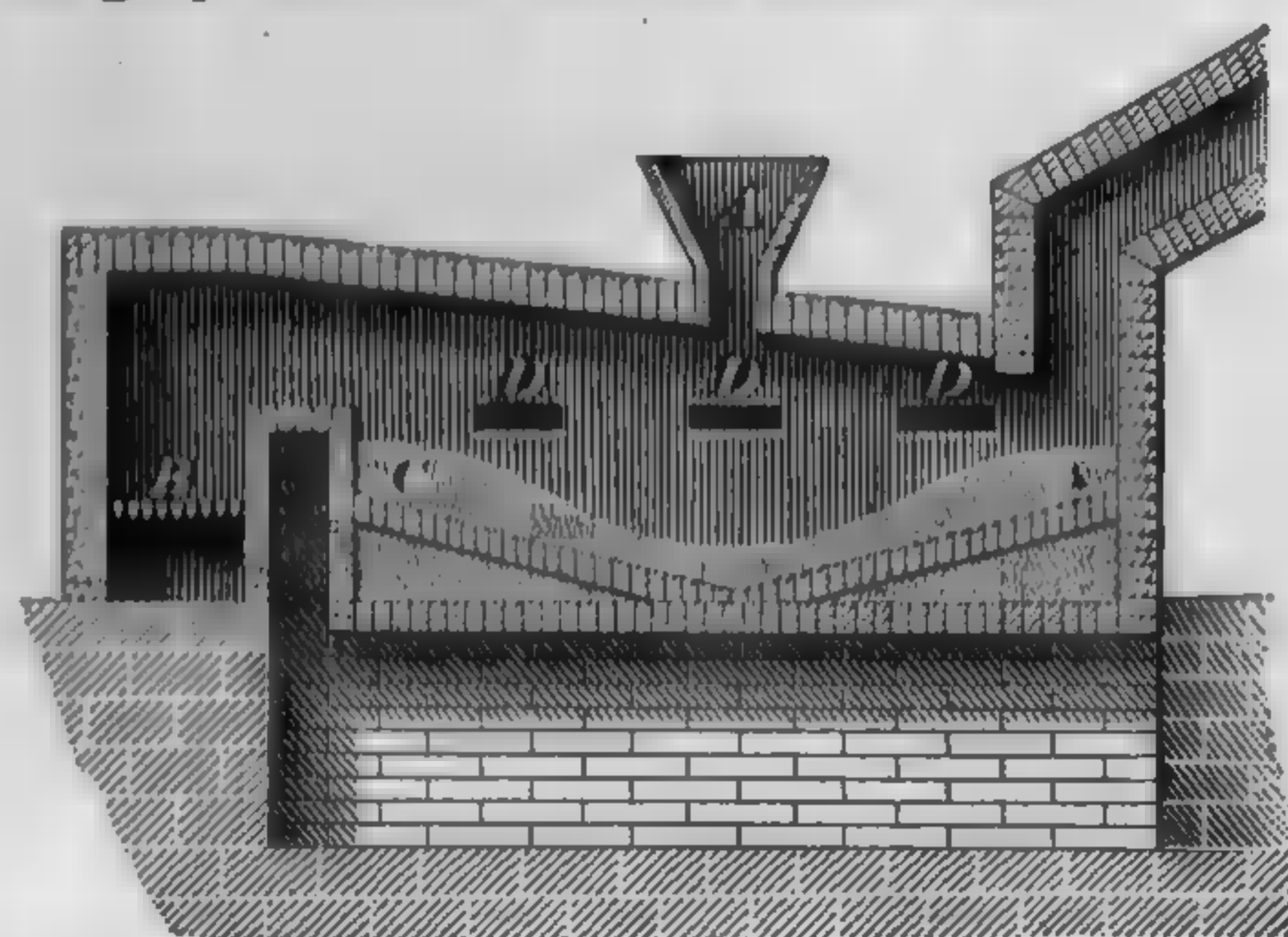


FIG. 2

from the foregoing in that the hearth is shallow and a blast is provided. The success of the process depends on the proper admixture of the fresh ore with that which has undergone oxidation, and in the regulation of the supply of air and fuel. The changes consist partly

in those described previously, that is, the oxidation of part of the ore and the double decomposition that takes place between this and the fresh ore, and partly in reduction by the fuel added.

Fig. 3 shows, in section, this form of hearth; its essential parts are: The hearth *A*, about 4 to 6 inches deep; the work stone *B*, provided with a shallow rim and a diagonal groove for running off the lead; the pot *C*, for the reception of the metal; the tuyère *D*, at the back of the hearth, for providing the blast. Slags are usually worked up separately in a furnace of a similar type, but having a shaft, some 3 feet high, above the hearth in which the slag and fuel are placed as in a blast furnace.

The lead obtained by any of these processes frequently contains sufficient antimony, besides tin, copper, iron, silver, etc., to render it hard, in which case it is submitted to a process of *softening*. The metal is heated on the bed of a reverberatory furnace until the antimony, copper, etc. become oxidized and form a scum on the surface. This is skimmed off with litharge that collects with it, and the process continued until the lead shows the proper degree of softness.

18. The method most generally adopted at the present time is to reduce the lead in blast furnaces. This method is

suitable for ores containing lower percentages of lead than is necessary for the other process, and also for other ores containing gold and silver as well. Ores containing considerable sulphur are roasted and the roasted ore mixed with silicious and basic ores containing gold, silver, and small amounts of lead, copper, arsenic, antimony, iron, and bismuth. This mixture of ores is then

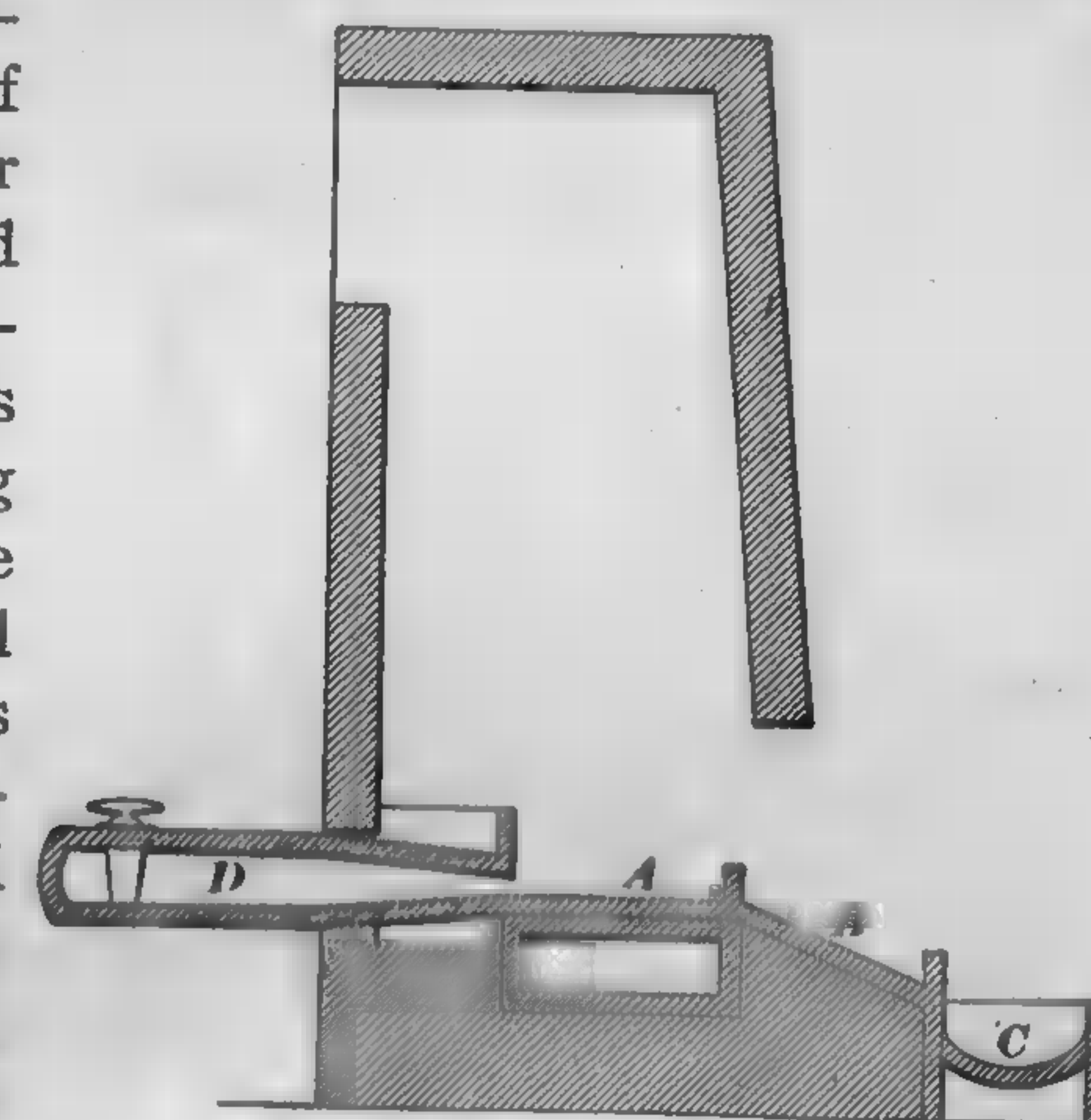


FIG. 3

charged into the blast furnace together with coke and limestone. The slag from a blast furnace usually contains from 30 to 40 per cent. silica, 30 to 40 per cent. iron, and 15 to 25 per cent. lime. The sulphur remaining in the ore unites with the iron and copper to form matte, and the gold, silver, and lead are collected together. The matte is recharged with fresh ore. From time to time the lead, silver, and gold is tapped into pots and transferred to a drossing kettle.

In the drossing kettle the molten metal is allowed to cool until it begins to harden on the edges, when the greater portion of the copper, arsenic, antimony, iron, and bismuth rise to the

surface and are skimmed off. After having been thoroughly drossed the temperature of the kettle is raised, the metal, or *base bullion*, is run in pigs, and sent to the refinery, where the gold and silver are separated from the lead.

19. Desilverizing Lead.—Among the many processes devised for the purpose of desilvering the lead the best known are the Pattinson, Rozan, and Parkes.

The *Pattinson process* depends on the fact that pure lead solidifies at a somewhat higher temperature than an alloy of silver and lead. By melting the lead and then allowing it to cool, the purer lead crystallizes out first; if this is removed by a perforated ladle, the liquid remaining is richer in silver. By repeating this treatment the silver accumulates, until a ton of the lead contains as much as 600 to 700 ounces of silver, after which the silver is best separated by *cupellation*.

The *Rozan process* is similar in principle, but the proper temperature is attained by the use of high-pressure steam and reduced by water. Much larger quantities can be acted on at the same time; there is the further advantage that the extreme agitation and contact with air promotes the removal of antimony and other impurities at the same time.

In the *Parkes process*, zinc is added to the metal in suitable proportions, an alloy of lead, zinc, and silver in this case solidifying, while the lead free from silver remains molten.

20. Cupellation.—For obtaining the silver free from lead, the metal is heated in an oxidizing atmosphere on a *cupel*, that is, in a special furnace, the bed of which is made of bone ash impregnated with pearl ash. The lead is oxidized to litharge, which collects at the surface of the charge and is blown off or to some extent absorbed by the bed of the furnace, carrying with it the impurities and leaving molten silver.

21. Properties.—Lead is a soft, brilliant, bluish-white metal that leaves on paper a bluish-gray streak, is very malleable and slightly ductile, and tarnishes in the air. It has a specific gravity of 11.37, crystallizes in regular octahedrons, fuses at 328° C., and volatilizes at a bright-red heat. At a white heat it may be distilled. It has but a feeble tenacity, a

wire 2 millimeters in diameter sustaining only a weight of 9 kilograms. Its freshly cut surface remains bright in perfectly dry air and also in water free from air. Potable waters in general act on lead, dissolving it, and partly precipitating it as carbonate. This action is particularly noticeable in well waters, which contain nitrates from decomposed animal matter, or chlorides from saline infiltration; lead water pipes should therefore be avoided, as a rule. When melted in the air, lead is rapidly converted into the oxide. It is scarcely attacked by sulphuric or hydrochloric acid at ordinary temperature, but dissolves readily in nitric acid. In presence of air and moisture it is acted on by quite feeble acids, such as acetic and carbonic acids; hence, the use of vessels made of lead or soldered with lead should be avoided for cooking vegetables, fruit, etc., which all contain more or less acid. When taken into the system, lead unites definitely with certain tissues and is retained there, until finally sufficient accumulates to produce poisoning. Acute colic is characteristic of poisoning by a large dose of lead, but in chronic poisoning, which is far more common, there is paralysis, particularly in the muscles of the forearm, causing the wrist to drop; or there may be simply an indefinable feeling of malaise, accompanied by dyspeptic symptoms.

22. Uses of Lead.—Lead is largely used in the manufacture of pipes for the distribution of water and gas, and, mixed with a small portion of arsenic, in the manufacture of shot. When reduced to sheets it is made into gutters, the covering of roofs, and lining for troughs and reservoirs. Alloyed with antimony and tin, it forms type metal; with bismuth, the soft alloy is used for permanent pencil points; with tin, it makes pewter and soft solder; and with tin, cadmium, and bismuth, a fusible metal which melts at 100° C.

COMPOUNDS OF LEAD

23. Lead oxide, PbO . occurs in nature as the mineral *massicot*. It is prepared on a large scale in the arts under the name of *litharge*, by heating melted lead in a current of

air. Its color is either pale yellow or orange yellow, according to the temperature at which it is prepared. It is dimorphous, crystallizing in rhombic octahedrons and in regular dodecahedrons; it fuses at red heat. Its specific gravity varies from 8.74 to 9.50. Acids dissolve it very readily, forming definite salts. It is only difficultly soluble in water, 7,000 parts of water being required to dissolve 1 part of lead oxide. It is soluble in alkali-hydroxide solutions as well as in lime water. Litharge is employed in the manufacture of glass, of lead acetate, and of white lead. It gives to linseed oil drying properties.

24. Lead hydroxide, $Pb(OH)_2$, is known only as a colorless, sweetish liquid, obtained by the action on lead of water and air, free from carbon dioxide. The precipitate produced by hydroxides of the alkalies in lead solutions is usually a compound having the composition $Pb_2O(OH)_2$.

25. Lead peroxide, PbO_2 , is obtained as a brown powder by treating *minium*, or *red lead*, with dilute nitric acid and washing the precipitate with boiling water. Lead peroxide is insoluble in water; it is readily decomposed by heat, losing half its oxygen and being converted into lead oxide. It is an energetic oxidizing agent. When it is briskly triturated with sulphur, the latter is inflamed. If it is introduced into a test tube with sulphur dioxide, the latter is immediately absorbed, with formation of lead sulphate:



Digested with ammonium hydroxide, it forms water and lead nitrate; it sets iodine free from potassium iodide, and bleaches a solution of sulphindigotic acid. It combines directly with the oxides of potassium, sodium, calcium, and even lead, forming salts called *plumbates*, having the general formula M_2PbO_3 , in which *M* stands for a univalent metal.

26. Lead sesquioxide, Pb_2O_3 , is obtained as a reddish-yellow powder, by mixing lead acetate and sodium hydroxide, and adding sodium hypochlorite to this solution. Its constitution

has not been determined with certainty, but it is most likely a salt of plumbic acid, $PbO(OH)_2$, having the formula $Pb \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \\ \diagup O \diagdown \end{array} Pb$, or $PbO_2 \cdot PbO$.

27. Red lead, or minium, Pb_3O_4 , is obtained by gently heating lead oxide in the air, thus causing it to take up oxygen. The commercial article varies somewhat in composition, and its color varies slightly according to the method of preparation. Its constitution is not positively known, but it is most likely a salt of normal plumbic acid, $Pb(OH)_4$, having the formula

$Pb \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \\ \diagup O \diagdown \\ \diagdown O \diagup \end{array} Pb$, or $2PbO \cdot PbO_2$. It is used as a pigment, and sometimes as a flux in the manufacture of glass, porcelain, etc. It is soluble in glacial acetic acid and in hydrochloric acid.

28. Lead sulphide, PbS , occurs as *galena* in nature in beautiful cubical crystals of a bluish-gray color and a metallic luster; its specific gravity is 7.25 to 7.70. It melts at red heat. When heated in contact with air, it is converted into oxide and sulphate, and, by the action of an excess of sulphide on these compounds, metallic lead is produced. Hot, fuming nitric acid converts lead sulphide into sulphate. Concentrated and boiling hydrochloric acid transforms it into chloride, with evolution of hydrogen sulphide. Lead sulphide is obtained as a black precipitate by leading hydrogen sulphide into a lead solution; it is prepared also by fusing lead and sulphur together.

29. Lead chloride, $PbCl_2$, has been found in the crater of Vesuvius after an eruption, and is known as *cotunnite*. It is precipitated from any lead solution, if sufficiently concentrated, on the addition of hydrochloric acid or a chloride. It is a heavy, white powder, soluble in 135 parts of cold and 30 parts of boiling water, from which it crystallizes, on cooling, in lustrous needles. It melts when heated in closed vessels, and at a higher temperature sublimes. The fused chloride is translucent and sectile, and is known as *horn lead*. White and

yellow oxychlorides are used as pigments, variously known as *mineral yellow*, *Turner's yellow*, and *Cassel yellow*.

30. Lead tetrachloride, $PbCl_4$, is formed by passing chlorine into concentrated hydrochloric acid containing lead chloride, until it is saturated, and then adding ammonium chloride, when yellow crystals of $PbCl_4 \cdot 2NH_4Cl$, or $Pb(NH_4)_2Cl_6$, separate. When treated with ice-cold sulphuric acid, these crystals are decomposed into hydrochloric acid, ammonium sulphate, and lead tetrachloride, the latter separating as an oily liquid. Lead tetrachloride crystallizes at $-15^\circ C.$, has a specific gravity of 3.18, and is decomposed into chlorine and the dichloride at ordinary temperature. At $105^\circ C.$ it decomposes with explosive violence.

31. Lead iodide, PbI_2 , is obtained as a beautiful yellow precipitate when a solution of potassium iodide is added to a solution of a lead salt. This compound melts to a red-brown liquid at high temperature. Lead iodide is soluble in 1,235 parts of cold and 194 parts of boiling water. On the cooling of its saturated, boiling solution, it is deposited in golden-yellow, hexagonal scales having a magnificent luster.

32. Lead nitrate, $Pb(NO_3)_2$, is prepared by dissolving lead, or its oxide or carbonate, in dilute nitric acid, from which it crystallizes in white, regular octahedrons. The crystals dissolve in $7\frac{1}{2}$ times their weight of cold water, and in a much less quantity of boiling water. At a red heat this salt is decomposed into nitrogen peroxide, oxygen, and lead oxide. It has an astringent taste, and decrepitates when heated. It is used in the manufacture of matches, in dyeing, and for the preparation of other lead salts.

33. Lead sulphate, $PbSO_4$, occurs in nature in rather small amounts. It is obtained as a heavy white precipitate by adding sulphuric acid or a soluble sulphate to a solution of a lead salt. It is practically insoluble in water, but dissolves slightly in strong sulphuric acid; nitric and hydrochloric acids dissolve it somewhat more freely. It dissolves readily in some ammonium salts, as the tartrate and acetate. It melts at a

red heat without undergoing decomposition. It is used in the preparation of rapidly drying oil varnishes, and frequently as a pigment in place of white lead.

34. Lead carbonate, $PbCO_3$, or basic carbonates of variable composition are precipitated when sodium carbonate is added to a solution of lead nitrate. The basic carbonate known as *white lead* is of great importance as a white pigment. If a solution of lead acetate is boiled with lead oxide and then filtered, a basic acetate is obtained, and on passing carbon oxide through the solution a white precipitate of this basic carbonate, essentially, $Pb_3(OH)_2(CO_3)_2$ is deposited. Prepared in this way, however, the pigment is denser and does not possess the same covering power as that formed more gradually by the so-called *Dutch process*. In this process coils of sheet lead are placed in conical earthenware vessels, Fig. 4, resting on a ledge, the bottom of the vessel containing weak acetic acid. These vessels, which are about 8 inches high, are stacked in layers, which are covered with tan bark or other fermenting vegetable matter; these stacks are about 15 feet square and 20 feet high. The heat generated by the fermentation gradually volatilizes the acetic acid and brings it into contact with the lead, and at the same time the carbon dioxide formed during the fermentation reacts with the basic acetate, yielding the basic lead carbonate. The acetic acid is then free to act on a further portion of lead, and the process repeats itself until practically the whole of the lead is transformed into *white lead*.

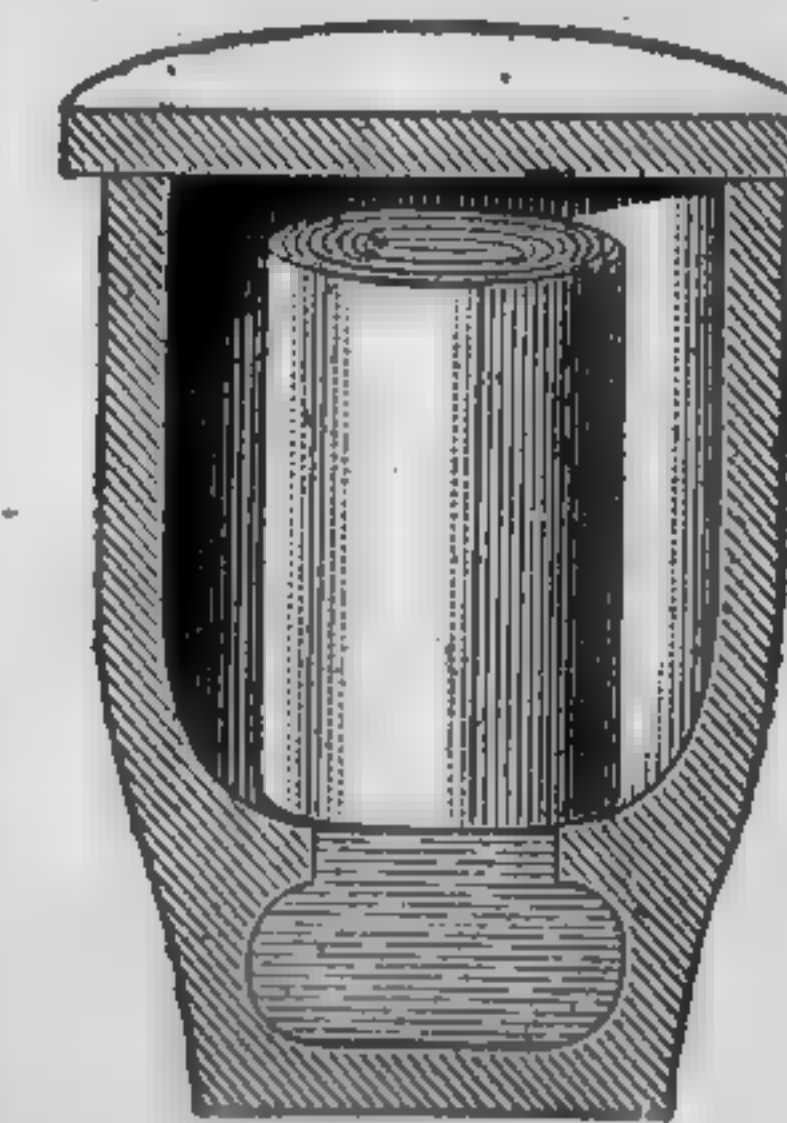


FIG. 4

35. Lead chromate, $PbCrO_4$, is found crystallized in nature, constituting the mineral *crocoisite*. It is obtained as a yellow precipitate by adding potassium chromate to the solution of a lead salt. Lead chromate gives up oxygen readily when heated in the presence of oxidizable substances. It dissolves quite readily in solutions of alkali hydroxides. It is used as a pigment under the name of *chrome yellow*, and is sometimes employed as an oxidizing agent in the analysis of organic substances.

FAMILY 5, GROUP A

GENERAL REMARKS

36. Family 5, Group A, consists of the rare elements *vanadium, columbium, tantalum, and didymium*. Of these, vanadium has probably been most thoroughly studied, though considerable work has also been done on columbium. These elements are all quite closely related to the members of Group B of the same family.

VANADIUM

Symbol V. Atomic weight 51. Valence II, III, and V.

37. Occurrence and Preparation.—Vanadium occurs in nature in the form of vanadates, which are analogous to phosphates. It has been found in clay, coal, and some rare minerals. Its principal minerals are *vanadinite*, $3\text{Pb}_3\text{V}_2\text{O}_8 \cdot \text{PbCl}_2$; *dechenite*, $\text{PbVO}_3 \cdot \text{ZnVO}_3$; *descloizite*, $\text{Pb}_2\text{V}_2\text{O}_7$; and *mottramite*, $(\text{CuPb})_5\text{V}_2\text{O}_{10} \cdot 2\text{H}_2\text{O}$. The method of obtaining vanadium is to digest the ore with hydrochloric or nitric acid and filter off the acid solution. This solution, together with the washings, is evaporated with an excess of ammonium chloride, when ammonium vanadate is precipitated; this is purified by crystallization. The ammonium vanadate is then gently roasted, forming vanadium pentoxide.

Another method is to fuse the ore with potassium nitrate, converting the vanadium into potassium vanadate. A salt of lead or barium is added to the solution of potassium vanadate and the precipitate obtained is decomposed with sulphuric acid. The vanadic acid formed is neutralized with ammonium hydrate, and the ammonium vanadate precipitated by means of ammonium chloride, in which it is insoluble. This is then

converted into the pentoxide by ignition. The metal is obtained by igniting the dichloride in a stream of hydrogen.

38. Properties.—Vanadium is a grayish-white, non-magnetic powder having a specific gravity of 5.5. It is neither fusible nor volatile when heated in hydrogen. Heated in oxygen it burns with a brilliant display of sparks, forming the oxide. It is insoluble in hydrochloric acid, and is only slowly soluble in strong, hot sulphuric acid. Metallic vanadium is harder than steel and precipitates platinum, gold, and silver from solutions of their salts. It is used to some extent in the manufacture of steel.

39. Compounds of Vanadium.—The *oxides* of vanadium recall those of nitrogen; they are *suboxide*, V_2O ; *monoxide*, V_2O_2 ; *trioxide*, V_2O_3 ; *dioxide*, V_2O_4 ; and *pentoxide*, V_2O_5 . With chlorine, vanadium forms the compounds VCl_2 , VCl_3 , and VCl_4 . The vanadates are derived from ortho-, meta-, and pyro-vanadic acids, which are similar to the acids of phosphorus in structure. Of these, the metavanadates are the most stable. These are derived from the acid HVO_3 , which is a golden-yellow compound sometimes used in place of gold bronze.

Orthovanadic acid, H_3VO_4 , is the final product of the oxidation of vanadium.

An *oxychloride*, VOCl_3 , corresponding to phosphorus oxychloride, is known.

COLUMBIUM

Symbol Cb. Atomic weight 93.5. Valence V.

40. Occurrence, Preparation, and Properties. Columbium, which is also sometimes called *niobium*, is found principally in the mineral *columbite*, though it also occurs in *euxenite*, *pyrochlore*, and some other rare minerals. It may be obtained by passing the vapor of columbium chloride, mixed with hydrogen, through a red-hot tube. It is a steel-gray element, having a metallic luster and a specific gravity of 7.1. On ignition in the air it burns readily to the pentoxide. It is

insoluble in hydrochloric, nitric, or nitrohydrochloric acids, but is soluble in hot sulphuric acid.

41. Compounds of Columbium.—There are three oxides of columbium, Cb_2O_2 , Cb_2O_4 , and Cb_2O_5 . The pentoxide, Cb_2O_5 , may be reduced to the tetroxide, Cb_2O_4 , by heating it strongly in hydrogen, but when this is heated in the air it is again oxidized to the pentoxide. With chlorine, columbium forms two compounds, $CbCl_3$ and $CbCl_5$.

A bromide having the formula $CbBr_5$, and a fluoride, CbF_5 , are known. The fluorides combine with fluorides of other metals, forming fluocolumbates of the general form M_2CbF_7 . The columbates are derived from a number of forms of the acid, all of which are closely related to the ortho-acid, H_3CbO_4 .

TANTALUM

Symbol Ta. Atomic weight 181.5. Valence V.

42. Occurrence and Preparation.—Tantalum occurs in nature in the minerals *columbite*, *tantalite*, and some other rare minerals. It obtained its name from the difficulty of separating it from its combinations. Berzelius prepared it by heating potassium fluotantalate with potassium, but Von Bolton obtained it pure by heating the product obtained as did Berzelius in an electric furnace in a vacuum. It is a silver-white metal, as hard as steel, is ductile and malleable when hot; its specific gravity is 16.6, and its melting point is $2,250^\circ C$.

43. Compounds of Tantalum.—There are two oxides of tantalum, Ta_2O_4 and Ta_2O_5 . With the halogens it forms the penta compounds, TaF_5 , $TaCl_5$, $TaBr_5$, and TaI_5 . Tantalum fluoride unites readily with fluorides of the other metals, forming fluotantalates of the general formula M_2TaF_7 . Thus, by treating tantalum fluoride with a solution of potassium fluoride, potassium fluotantalate, K_2TaF_7 , is obtained.

The tantalates are derived from *metatantallic acid*, $HTaO_5$, or *hexatantallic acid*, $H_5Ta_6O_{19}$, both of which appear to be derived from *orthotantallic acid*, H_3TaO_4 , by the loss of water.

PRASEODYMIUM

Symbol Pr. Atomic weight 140.6. Valence III.

44. Occurrence and Preparation.—At one time the substance known as didymium was supposed to be an element. This substance was found in cerite and in monazite sand. It was separated from cerium and lanthanum by Mosander in 1840, and by him reported as an element. Welsbach, in 1885, by making several thousand fractionations of didymium nitrate, obtained a pale-green salt and a rose-colored salt, which gave different spectra from the original salt, but which, when united, gave the spectrum of didymium. Praseodymium may be prepared by the electrolysis of the chloride. It has a yellow color, melts at $940^\circ C$., has a specific gravity of 6.5, and is unaffected by the air.

45. Compounds of Praseodymium.—A dioxide, PrO_2 , and a trioxide, or sesquioxide, Pr_2O_3 , are known. The dioxide PrO_2 is obtained as a black powder by heating a mixture of the nitrate with potassium nitrate to about $425^\circ C$. The sesquioxide Pr_2O_3 is obtained as a light green powder by heating one of the intermediate oxides in hydrogen. Praseodymium also forms a hydroxide, $Pr(OH)_3$, a chloride, $PrCl_3$; a sulphate, $Pr(SO_4)_3$; and a nitrate, $Pr(NO_3)_3$. The hydroxide is a pale-green powder, whereas the remaining compounds form pale-green crystalline salts.

NEODYMIUM

Symbol Nd. Atomic weight 144.3. Valence III.

46. Neodymium salts occur with samarium salts and are separated from the latter by fractional precipitation. It has a yellow color, melts at $840^\circ C$., and is slowly acted on by the air. Its chemical properties resemble those of praseodymium very closely. It has a specific gravity of 6.95. One stable oxide, the sesquioxide, Nd_2O_3 , and an unstable dioxide, NdO_2 , are known. The salts of neodymium are prepared from the sesquioxide and are rose colored.

FAMILY 6, GROUP A

INTRODUCTION

47. Family 6, Group A, consists of the elements *chromium*, *molybdenum*, *tungsten*, and *uranium*, which form the oxides CrO_3 , MoO_3 , WO_3 , and UO_3 , and the acids H_2CrO_4 , H_2MoO_4 , H_2WO_4 , and H_2UO_4 . In these compounds they closely resemble the members of Group B; but when they lose oxygen they form compounds that have little or no acid character. As the lower oxides of chromium are basic, there are a large number of salts in which chromium acts as a base. Molybdenum and tungsten do not appear to possess basic properties and form very few salts. Uranium acts in a rather peculiar manner; it enters into compounds combined with 2 atoms of oxygen, as the compound UO_2 , which acts like a bivalent metal, forming uranyl salts; thus the sulphate is UO_2SO_4 . These salts appear to be derived from a base $\text{UO}_2(\text{OH})_2$, but this compound also has distinct acid properties. Chromium is the most important member of this group, and will be treated first.

CHROMIUM

Symbol *Cr*. Atomic weight 52.0. Valence II, III, and VI.

48. History and Occurrence.—Chromium was discovered in 1797 by Vauquelin, in a mineral from Siberia, known as *crocoisite*, which is a chromate of lead. It derives its name from a Greek word meaning "color," in allusion to the varied colors of its compounds, on which their uses in the arts largely depend. It occurs in nature in the mineral *chromite*, or *chrome iron*, a combination of chromium oxide and ferrous oxide, probably a ferrous salt of metachromous acid, HOCrO_2 ,

having the formula $\text{Fe} \begin{matrix} \diagup \text{O} - \text{Cr} = \text{O} \\ \diagdown \text{O} - \text{Cr} = \text{O} \end{matrix}$. It also occurs as lead chromate in the mineral *crocoisite* and imparts the color to the emerald, and is found in meteoric iron.

49. Preparation and Properties.—Chromium may be prepared by decomposing chromic chloride by means of sodium in the form of vapor, by treating the chloride with zinc, or by electrolyzing it. It may also be prepared by mixing chromic oxide with powdered aluminum and igniting the mixture. Chromium is a light-gray, or tin-white, lustrous, crystalline substance. It is very hard and difficult to fuse, and oxidizes very slowly when heated in the air, but heated in oxygen or in the oxyhydrogen flame, it burns to chromic oxide, Cr_2O_3 . It is insoluble in nitric acid, but dissolves in hydrochloric and hot sulphuric acids. Its specific gravity is 6.81, and its melting point is $1,515^\circ \text{C}$. It is non-magnetic. Large quantities are used in the form of an alloy, *ferrochrome*, containing between 60 and 70 per cent. of chromium. These ferrochromes are used to introduce chromium into steel, thereby greatly increasing the hardness of the steel.

COMPOUNDS OF CHROMIUM

50. Hydroxides of Chromium.—*Chromous hydroxide*, $\text{Cr}(\text{OH})_2$, is obtained as a light-brown precipitate when potassium hydroxide is added to a solution of chromous chloride. It readily gives up water and hydrogen and is converted into *chromic oxide*, Cr_2O_3 .

Chromic hydroxide, $\text{Cr}(\text{OH})_3$, is obtained as a light-blue precipitate by adding ammonia to a solution of a chromic salt, and carefully drying the precipitate thus formed in a vacuum. When heated, this decomposes first into CrOOH and finally into Cr_2O_3 . Sodium and potassium hydroxides dissolve chromic hydroxide with the formation of the corresponding chromites, which are derivatives of the acid CrOOH . When solutions containing these chromites are boiled, chromic hydroxide is precipitated, but this precipitate always contains some of the alkali metal in combination.

51. Chromic oxide, or chromium sesquioxide, Cr_2O_3 , may be prepared by heating either of the hydroxides, but is more readily obtained on a large scale by heating a mixture of potassium dichromate and sulphur when potassium sulphate and chromic oxide result. Obtained in this way, it is a green powder that becomes almost insoluble in acids when heated. It is used in coloring glass and in china painting.

52. Chromium trioxide, CrO_3 , may be prepared by treating a concentrated solution of an alkali chromate or dichromate with concentrated sulphuric acid, when the trioxide crystallizes from the solution in fine red needles. It is deliquescent, and when dissolved in water gives an acid solution, which, when neutralized, yields chromates, thus indicating that the solution contains chromic acid, H_2CrO_4 . When heated, the trioxide gives up half its oxygen and is converted into chromic oxide. It is a powerful oxidizing agent and is reduced by almost any oxidizable substance.

53. Chromous chloride, $CrCl_2$, may be obtained by reducing chromic chloride by hydrogen at a moderate heat. It is a white, crystalline substance, soluble in water, forming a blue solution that, by absorption of oxygen, rapidly changes its color to green.

54. Chromic chloride, $CrCl_3$, is the most important compound of chromium and chlorine. It may be obtained by passing chlorine gas over an ignited and perfectly dry mixture of chromium and charcoal. A sublimate of brilliant, peach-blossom-colored scales is thus obtained, which is almost insoluble in cold and only sparingly soluble in boiling water, forming with the latter a green solution.

It may be prepared in solution by dissolving chromic hydroxide in hydrochloric acid. This solution has a deep green color, and when sufficiently concentrated deposits crystals having the composition $CrCl_3 \cdot 6H_2O$. When these crystals are heated in the air, they are decomposed with the formation of chromic oxide, but if heated in an atmosphere of chlorine or hydrochloric acid the water is expelled and the reddish-violet anhydrous chloride remains. This dissolves in water, forming a green solution,

but if first sublimed it becomes almost insoluble in water and acids. With the chlorides of the alkalis it forms double salts, as examples of which may be mentioned $KCrCl_4$ and K_2CrCl_6 .

55. Chromium oxychloride, or chromyl chloride, CrO_2Cl_2 , is obtained by heating a previously fused mixture of common salt and potassium dichromate with sulphuric acid; abundant red vapors are disengaged, and condensed to a blood-red liquid. It boils at $116.8^\circ C$. On contact with water it decomposes into hydrochloric acid and chromic acid.

56. Chromium sulphate, $Cr_2(SO_4)_3$, may be prepared in solution by dissolving chromic hydroxide in sulphuric acid. If the solution is allowed to evaporate slowly, it will deposit the sulphate in purple crystals having the composition $Cr_2(SO_4)_3 \cdot 15H_2O$, but if the solution is first boiled it turns green and the sulphate will not crystallize from it. If, however, the green solution is allowed to stand for some time it becomes purple again and purple crystals of sulphate separate. It appears to be true of the solutions of chromium salts in general that they exist in two modifications: a purple modification from which crystals are readily obtained, and a green variety, obtained by boiling the purple form, from which crystals cannot be obtained. The green solution changes back to purple if allowed to stand for some time.

57. Chrome Alum.—Like aluminum sulphate, chromium sulphate combines with the sulphates of the monovalent metals, forming double sulphates that crystallize from solution with 12 molecules of water. The most important of these, the double sulphate of chromium and potassium, known as *chrome alum*, has the formula $KCr(SO_4)_2 \cdot 12H_2O$. It is prepared by reducing a solution of potassium dichromate containing sulphuric acid, by means of sulphur dioxide. Neglecting the water of crystallization, which is furnished by the solution, the equation representing its formation may be written:

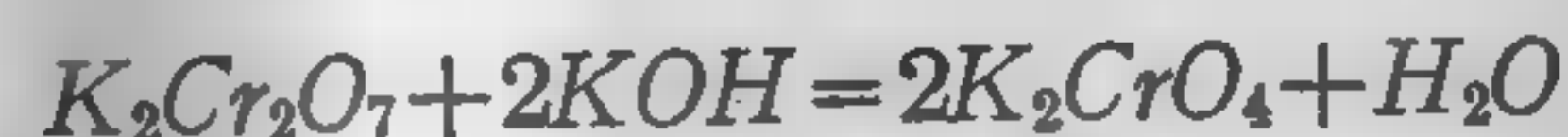


Chrome alum is used in tanning and dyeing, and to a slight extent in photography.

58. Chromic Acid and Chromates.—Chromous compounds when exposed to the air or treated with oxidizing agents, are readily oxidized to chromic compounds, which is the limit of oxidation if an acid is present. In these compounds chromium acts as a base and is usually regarded as such. If, however, the oxidation is carried out in the presence of a strong base, it proceeds further, and a chromate results. In these compounds chromium plays the part of an acid-forming element, and the chromates are derived from the hypothetical chromic acid, H_2CrO_4 . This acid has not been obtained in the free state, as it breaks up into chromium trioxide and water when set free from its compounds, just as do carbonic and sulphurous acids. It is believed that these acids exist in aqueous solution, for when chromium trioxide is dissolved in water and the solution is neutralized by a base, a chromate is formed. The chromates in general resemble the sulphates; probably chromic acid is similar in structure to sulphuric acid, and should be represented by the formula $\begin{matrix} HO & \diagdown & O \\ & Cr & / \\ HO & \diagup & O \end{matrix}$. It has been stated that sulphuric acid loses water and forms pyrosulphuric or disulphuric acid. In the same way, theoretically, chromic acid is converted into dichromic acid. Neither of these acids exists in the free state, but in all probability the relation between chromates and dichromates is the same as between sulphates and disulphates. By treating a chromate with an acid, a dichromate is obtained. Thus, if potassium chromate is treated with nitric acid the following reaction takes place:



On the other hand, if a dichromate is treated with an alkali hydroxide, a chromate results. This may be illustrated by the equation:



59. Potassium chromate, K_2CrO_4 , is obtained by adding potassium hydroxide to the solution of the dichromate. It crystallizes in yellow rhombic crystals, is permanent in the air, has a cooling taste, and an alkaline reaction. It dissolves

very easily in water and is therefore difficult to purify; for this reason it is usually converted into the dichromate, which is readily purified.

60. Potassium dichromate, $K_2Cr_2O_7$, is prepared from chromite. The chromite is roasted and is then ground and mixed with potassium carbonate and lime and heated. Calcium and potassium chromates are formed, and these are dissolved in water. Potassium sulphate is added to the solution, when calcium sulphate is precipitated and all the chromium is converted into potassium chromate. The solution is then treated with the proper amount of sulphuric acid, thus converting the chromate into the dichromate. As it dissolves in 10 parts of water at ordinary temperature, and is much more soluble in hot water, it crystallizes, on cooling, in large red plates belonging to the triclinic system. As the dichromate crystallizes well, it is easily purified by recrystallization. The chromate and dichromate may be regarded as the starting point for the preparation of the other compounds of chromium. When heated, the dichromate fuses without decomposing, but at a higher temperature it breaks up into potassium chromate, chromic oxide, and oxygen. When heated with sulphuric acid, the potassium and chromium unite with the acid, forming chrome alum. Water is also evolved, and all the oxygen not used in the formation of these is set free.

Potassium dichromate is largely used as an oxidizing agent. It is also used in dyeing, and to a certain extent in photography, and as the starting point for the preparation of nearly all the other chromium compounds.

61. Sodium chromate, Na_2CrO_4 , is obtained just as is potassium chromate; and by treating it with an acid, *sodium dichromate, $Na_2Cr_2O_7$,* is obtained. These compounds closely resemble the corresponding potassium salts, and are now used extensively in place of the more expensive potassium compounds.

62. Barium chromate, $BaCrO_4$, is obtained as a yellow precipitate when a soluble chromate is added to the solution of a barium salt. It is insoluble in water and in acetic acid,

but dissolves in nitric and hydrochloric acids. It is used somewhat as a pigment under the name of *lemon yellow*.

63. Lead chromate, $PbCrO_4$, occurs in nature as crocoisite. It may be prepared by adding a soluble chromate or dichromate to the solution of a lead salt, when the chromate separates as a yellow precipitate that is used as a pigment under the name of *chrome yellow*. When treated with a small quantity of a dilute solution of a hydroxide, it turns red, owing to the formation of basic lead chromate, Pb_2OCrO_4 , known as *chrome red*. This is used in dyeing, by dyeing the substance in chrome yellow and then dipping it in a bath of lime water, when the chrome yellow is changed to chrome red, and the substance is consequently dyed red.

64. Silver chromate, Ag_2CrO_4 , is formed as a brick red precipitate when a solution of silver nitrate is treated with a solution of potassium chromate. The dichromate is obtained when potassium dichromate is added to a slightly acid solution of silver nitrate. It forms small scarlet triclinic crystals.

MOLYBDENUM

Symbol Mo. Atomic weight 96.0. Valence II, III, IV, and VI.

65. Occurrence and Properties.—Molybdenum occurs principally as sulphide, or *molybdenite*, MoS_2 , as lead molybdate, or *wulfenite*, $PbMoO_4$, and frequently as *molybdenum ochre*, MoO_3 . It is prepared by reducing the oxides or chlorides of molybdenum by a current of hydrogen at a high temperature. It is a white, very hard, brittle metal, and is almost infusible. It has a specific gravity of 8.56, and oxidizes, when heated in the air, to molybdenum trioxide. It forms four oxides: MoO , Mo_2O_3 , MoO_2 , and MoO_3 .

COMPOUNDS OF MOLYBDENUM

66. Oxides.—*Molybdenum trioxide, MoO_3 ,* frequently called *molybdic acid*, is obtained by roasting at a moderate temperature the natural molybdenite, MoS_2 ; the resulting oxide is dissolved

in ammonia and the solution filtered. On evaporation and cooling, crystals of ammonium molybdate are obtained, which yield molybdenum trioxide when strongly heated in the air. Molybdenum trioxide is a white, fusible, volatile powder; it is only slightly soluble in water, its solution being acid.

Molybdic oxide, Mo_2O_3 , is formed as a black precipitate when a solution of the trioxide is treated with a reducing agent, such as sodium amalgam.

Molybdenum dioxide, MoO_2 , is obtained by gently heating molybdenum or molybdic oxide in the air. It is a dark-blue compound.

Molybdenum monoxide, MoO , is obtained as a black precipitate, by treating a solution of molybdenum dichloride with a hot solution of potassium hydroxide.

67. Sulphides of Molybdenum.—*Molybdenum disulphide, MoS_2 ,* occurs in nature as molybdenite; it thus occurs in masses of tabular crystals that possess a strong metallic luster and steel-gray color and leave a gray streak on paper, similar to graphite. The same compound is produced artificially by heating the trisulphide or by igniting the trioxide with sulphur. When roasted in contact with the air, it is converted into trioxide.

The *trisulphide, MoS_3 ,* is obtained by passing hydrogen sulphide into a concentrated solution of a molybdate in the presence of hydrochloric acid. It is a reddish-brown powder that is slowly dissolved by alkalis, more easily by alkaline sulphides, forming sulphur salts called *thiomolybdates*. The thiomolybdates of the alkaline metals, alkaline earths, and magnesium are soluble in water, forming solutions of a fine red color.

68. Chlorides of Molybdenum.—Molybdenum forms four chlorides, the formulas of which appear to be $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$.

The *pentachloride, $MoCl_5$,* is obtained when pure metallic molybdenum is heated for some time in a stream of chlorine. If this pentachloride is heated to about $250^\circ C$. in a stream of hydrogen it is reduced to the red, difficultly volatile *trichloride*,

MoCl_3 ; this compound heated to redness in an atmosphere of carbon dioxide free from oxygen, is resolved according to the equation $2\text{MoCl}_3 = \text{MoCl}_2 + \text{MoCl}_4$ into the yellow *dichloride*, which remains in the tube, and the brown *tetrachloride*, which either sublimates or is carried forward by the stream of gas. Of these four chlorides the pentachloride is the only one that crystallizes distinctly, and melts and volatilizes without decomposition. The pure pentachloride is black, and its vapor has a dark, brown-red color. The yellow dichloride and the red trichloride, which latter closely resembles amorphous phosphorus, have both been obtained in the amorphous state. In an atmosphere of carbon dioxide, the dichloride bears a bright-red heat without melting or volatilizing; the trichloride, under the same circumstances, is resolved into dichloride and tetrachloride, which, when again heated, splits up into pentachloride, which sublimes, and trichloride, which remains behind.

The dichloride and trichloride are permanent at ordinary temperatures in the atmosphere and insoluble in water; the tetra and pentachlorides, on the other hand, are rather unstable, being very susceptible to the action of oxygen and moisture. The dichloride is insoluble in nitric acid, which readily dissolves all the other chlorides. The dichloride dissolves easily, when heated with hot hydrochloric acid, and crystallizes therefrom on cooling, in long, yellow lustrous needles.

The *bromides* of molybdenum are similar to the chlorides in composition.

69. Molybdic Acid.—It has been stated that molybdenum trioxide is sparingly soluble in water, giving an acid solution. If this solution is neutralized by bases, molybdates are formed that are similar to the chromates in composition. When the ammonium salt thus obtained is treated with dilute nitric acid it is decomposed, and **molybdic acid**, $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$, crystallizes out of the solution. A number of salts are derived from this acid; but as the acid has a great tendency to combine with itself, most of the salts are derived from polymolybdic acids. Molybdic acid also unites with other acids, forming complicated acids that unite with bases forming complex salts. The

best known of these acids is *phosphomolybdic acid*, a combination of phosphoric and molybdic acids. When phosphoric acid or a soluble phosphate is added to a solution of ammonium molybdate in an excess of nitric acid, a yellow precipitate of ammonium phosphomolybdate separates; this is a salt of phosphomolybdic acid, the formula of which is generally written $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_{12}$, though its structure is not thoroughly understood.

TUNGSTEN

Symbol W. Atomic weight 184.0. Valence II, IV, and VI.

70. Occurrence and Preparation.—Tungsten occurs in nature in a few minerals. Its symbol, *W*, is derived from the mineral *wolframite*, which is tungstate of iron and manganese, and from which it was first obtained; it occurs in *scheelite*, which is calcium tungstate; in *stolzite*, which is lead tungstate; etc. Metallic tungsten is obtained by reducing tungsten trioxide, WO_3 , with hydrogen or aluminum powder as an iron-gray metal of specific gravity 16.6 to 19.129. It is extremely hard, melts at $2,800^\circ \text{C}$., and is unaffected by either hydrochloric or sulphuric acid, though it is converted into tungstic acid by the action of nitric acid. When dissolved in about ten times its own weight of fused steel, tungsten forms an extremely hard alloy, known as *tungsten steel*, that is used in the manufacture of machinists' tools. One of the most peculiar properties of tungsten is its ability to increase the magnetic power of the steel with which it is alloyed. A horseshoe magnet of ordinary steel, weighing 2 pounds, for instance, is generally considered of very good quality if it bears seven times its own weight, but a similar magnet made of an alloy of steel and tungsten is able to bear nearly twenty times its own weight.

COMPOUNDS OF TUNGSTEN

71. Oxides.—*Tungsten dioxide*, WO_2 , appears to be a chemically indifferent oxide, and is obtained by reducing tungsten trioxide with hydrogen at a low red heat, when it forms a

brown powder that is dissolved by boiling in solution of potassium hydroxide, hydrogen being evolved, and potassium tungstate formed, according to the equation $2KOH + WO_3 = K_2WO_4 + H_2$.

Tungsten trioxide, WO_3 , is obtained by decomposing metallic tungstates with nitric acid, and heating the tungstic acid thus precipitated. It is a canary-yellow powder, becoming orange when heated and yellow again when cooled.

72. Chlorides.—*Tungsten hexachloride*, WCl_6 , is obtained as a bronze-colored substance when tungsten is heated in dry chlorine. It fuses at 275°C . and boils at 346°C .

The *pentachloride*, WCl_5 , is obtained as shining black crystals by distilling the hexachloride in a current of hydrogen or carbon dioxide. It melts at 248°C ., boils at 276°C ., is very hygroscopic, exposure to the air instantly covering the crystals with a golden-green film.

The *tetrachloride*, WCl_4 , is obtained by gently igniting WCl_6 , or WCl_5 , in an atmosphere of hydrogen. It is a grayish-brown substance. It is very hygroscopic, although not to quite the extent of the pentachloride, and is decomposed by cold water into the dioxide and hydrochloric acid.

The *dichloride*, WCl_2 , is obtained by strongly igniting WCl_6 in hydrogen. It is a bright, gray, non-volatile substance. Tungsten oxychlorides are also known.

73. Tungstic Acid.—When tungsten trioxide is fused with the proper amount of potassium carbonate, or solutions of these substances are mixed in the proper proportions, potassium tungstate, K_2WO_4 , is formed; if a solution of this compound is treated with a strong acid, **tungstic acid** is precipitated. If the solution is hot, the acid has the composition H_2WO_4 ; but if at ordinary temperature, the precipitate has the composition $H_2WO_4 \cdot H_2O$, corresponding to molybdic acid. Like molybdic acid, tungstic acid has a tendency to unite with itself, forming polytungstic acids, and with other acids, forming complex acids. These combine with bases, forming very complicated compounds.

URANIUM

Symbol U. Atomic weight 238.5. Valence II, IV, and VI.

74. Occurrence and Preparation.—The chief mineral used as a source of uranium is *pitchblende*, in which it occurs as U_3O_8 . When this is finely powdered and heated with sulphuric acid, the uranium is transformed partly into uranium sulphate, $U(SO_4)_2$, and partly into uranyl sulphate, UO_2SO_4 , both of which are readily soluble in water. The oxide, U_3O_8 , is used in coloring porcelain black, and other uranium compounds are used for pigments and in the manufacture of colored glass. That which was regarded as the metal from the time of the discovery of uranium by Klaproth, in 1789, until 1841, was in reality the dioxide, UO_2 . In that year Peligot showed that this contained oxygen by heating it mixed with charcoal in a current of chlorine gas, when carbon monoxide and dioxide were given off.

The pure metal may be prepared by strongly heating a mixture of the tetrachloride, UCl_4 , with metallic sodium covered with sodium and potassium chlorides. The experiment is carried out in a crucible enclosed in a second crucible containing charcoal, so as to insure the exclusion of air. It can be prepared also by heating the oxide U_3O_8 , in an electric furnace with about one-tenth its weight of charcoal prepared from sugar.

75. Properties.—Uranium is a white metal, capable of taking a high polish, and somewhat softer than steel, and is malleable. Its specific gravity is 18.7. It melts at a bright-red heat, and is permanent in the air. It combines directly with fluorine at ordinary temperatures; with chlorine, bromine, iodine, sulphur, and oxygen at a moderate heat; and with nitrogen at a bright-red heat. It decomposes water slowly at ordinary temperatures, and very rapidly at about 100°C . With carbon at high temperatures, it forms a carbide, U_2C_3 , that acts on water, forming a mixture of gaseous, liquid, and solid hydrocarbons. The metal and its salts are radioactive; all its salts are powerful poisons.

COMPOUNDS OF URANIUM

76. Oxides.—As stated, uranium occurs in nature in the form of the oxide, U_3O_8 , which is also the final product of the oxidation of uranium in the air. When this oxide is treated with nitric acid, uranyl nitrate is formed, and when this is heated, uranium trioxide is formed. The dioxide is formed by reducing the trioxide by means of hydrogen. When either of these oxides is ignited in the air, U_3O_8 results. This is believed

to be *uranus uranate*, having the composition $U \begin{array}{c} \diagup O \\ \diagdown O \end{array} \begin{array}{c} \diagup O \\ \diagdown O \end{array} \begin{array}{c} \diagup O \\ \diagdown O \end{array} UO_2$.

The *tetroxide*, UO_4 , is obtained as a light-yellow precipitate by adding hydrogen peroxide to a uranyl salt.

77. Chlorides.—*Uranium tetrachloride*, UCl_4 , is formed when chlorine acts on finely divided uranium, but this is usually accompanied by some pentachloride. By reducing this with hydrogen, the *trichloride*, UCl_3 , is obtained; and by heating the tetrachloride for some time in chlorine it is partially converted into the pentachloride. The *tetrachloride*, UCl_4 , is the most stable of the chlorides.

78. Uranous and Uranyl Salts.—The few uranous salts are derived from tetravalent uranium, 1 atom replacing 4 of hydrogen, as shown by the sulphate, $U(SO_4)_2$. In the uranyl compounds, the group UO_2 acts like a bivalent metal. The salts formed may be illustrated by the sulphate, UO_2SO_4 , and the nitrate, $UO_2(NO_3)_2$. These salts, it is evident, are derived from the hydroxide, $UO_2(OH)_2$, which acts as a base in the presence of acids.

79. Uranates.—It has just been shown that in the presence of acids, the hydroxide, $UO_2(OH)_2$, acts as a base. In the presence of some of the stronger bases it also acts as an acid. When a uranyl salt is acted on by an alkali hydroxide, a precipitate is formed having the composition $M_2U_2O_7$, and is therefore derived from an acid, $H_2U_2O_7$, which is analogous

to dichromic acid, and is known as diuranic acid. One of the most important derivatives of this acid is sodium diuranate, $Na_2U_2O_7$, a yellow powder that is manufactured in large quantities and used in coloring glass.

RADIOACTIVE ELEMENTS

80. It was discovered by Becquerel that uraninite emits a peculiar kind of rays. They move in a straight line, act on a photographic plate, and cannot be reflected or refracted. Gases become electrical conductors when these rays are passed through them. For a while it was thought that this radioactivity was due to the uranium present; but M. and Mme. Curie have proved that the radioactivity is caused by three hitherto unknown elements that they called *radium*, *polonium*, and *actinium*. The amounts of these elements present were very minute, and in order to separate them from the residues left after extracting the uranium, these were subjected to numerous chemical operations and the success in concentration judged by measuring the conductivity of an air layer exposed to the rays. It will be observed that for the discovery of these elements an entirely new method of testing was introduced.

Radium is the most thoroughly investigated of these elements and has been obtained nearly pure as chloride. It has an atomic weight, according to Mme. Curie, of 226.4. It accompanies the barium chloride extracted from uraninite and is separated from it by fractional crystallization, the radium chloride being less soluble than barium chloride. It has a characteristic spectrum resembling that of the alkaline earths. Radium compounds give light in the dark; when they are very concentrated they transform oxygen into ozone and have an odor like sodium hypochlorite. Under the influence of the rays emitted, glass assumes a brown color and potassium and sodium chlorides turn blue.

Polonium is found with bismuth extracted from uraninite; its chemical properties are similar to bismuth. The sulphide

is more volatile in vacuo than bismuth sulphide, which property is taken advantage of in separating it.

Actinium resembles thorium.

Our knowledge of these elements is very limited, and at present it is not possible to assign to them any definite place in the periodic system.

FAMILY 7, GROUP A

81. This group at present consists of the element *manganese*, which in some ways resembles the members of Group B of the same family; it acts principally as a base-forming element, and in many of its compounds resembles chromium.

MANGANESE

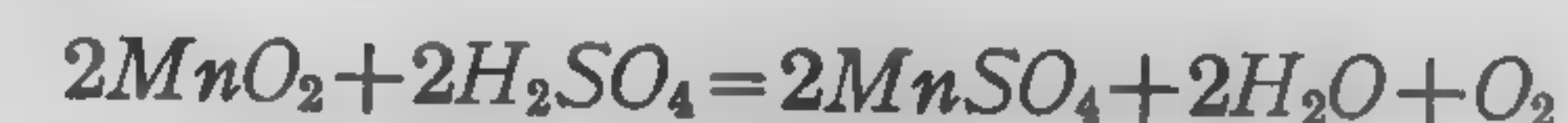
Symbol Mn. Atomic weight 54.93. Valence II, III, IV, VI, and VII.

82. *History and Occurrence.*—Manganese was discovered by Scheele and Bergmann in 1774, in a mineral known as *braunstein*. Owing to its being confounded with magnetic iron, this mineral had received the Latin name of this substance, that is, *magnesia nigra*; whence the name magnesium first was assigned to the new metal. This name was afterwards changed to manganese, to distinguish it from true magnesium obtained from the *magnesia alba*. It is found chiefly as *pyrolusite*, MnO_2 , *braunite*, Mn_2O_3 , and *rhodochrosite*, $MnCO_3$. Manganese sulphide, arsenide, and silicate are also known as minerals. The metal itself has not been applied to any very useful purpose in the arts, but forms some useful alloys.

Manganese is best prepared by reducing MnO_2 by means of aluminum powder. It is a grayish-white, hard, brittle metal, having a specific gravity of 8, is feebly magnetic, fuses at $1,245^\circ C.$, and volatilizes at the temperature of the electric furnace. It will take a high polish, but oxidizes readily in the air unless it contains iron. It decomposes water at but little above the ordinary temperature, is easily soluble in all dilute acids, and combines with carbon and nitrogen at a high temperature.

COMPOUNDS OF MANGANESE

83. *Manganese dioxide*, or *peroxide*, MnO_2 , the chief compound and most important one of manganese, occurs in nature as *pyrolusite* in amorphous masses, in crystalline masses, or in steel-gray, rhombic crystals. It has a metallic luster, a black streak, and is opaque and brittle. It contains about 90 per cent. of manganese and has a specific gravity of 4.8. Manganese dioxide is also found in the hydrated state as *wad*. *Pyrolusite* is frequently known as the *black oxide of manganese*. It is largely used in the manufacture of steel, although frequently replaced by alloys of iron and manganese such as *spiegeleisen* and *ferromanganese*, the manufacture of bleaching powder, in the making of glass, and as a source of oxygen. Manganese dioxide does not combine readily with acids, although hydrochloric acid dissolves it, giving a brown solution. If this solution is heated chlorine is evolved and the pink manganese chloride is obtained. Nitric acid has almost no action on the dioxide, but strong sulphuric acid dissolves it, evolving oxygen, thus:



Dilute sulphuric acid in the presence of some readily oxidizable substance, such as oxalic acid or ferrous sulphate, produces the same effect.

Heating with hydrogen does not reduce the oxides of manganese to metallic manganese but forms manganous oxide, MnO .

84. *Manganous oxide*, MnO , or *manganese monoxide*, is obtained by the preceding method, or by fusing a mixture of anhydrous manganese chloride, sodium carbonate, and ammonium chloride. It forms a green powder, which, when heated in hydrogen, crystallizes in emerald-green octahedra having an adamantine luster and a specific gravity of 5.1. It is soluble in acids, forming the manganous salts, absorbs oxygen from the air, and fuses at a white heat without loss of oxygen. It is found in nature as the mineral *manganosite*.

85. *Manganic oxide*, Mn_2O_3 , or *manganese sesquioxide*, occurs as the mineral *braunite* in octahedral crystals. It closely

resembles the dioxide, has a brownish-black color, a semi-metallic luster, and a specific gravity of 4.8. It is soluble in strong sulphuric acid, is feebly basic, and may be obtained by heating any of the oxides of manganese to redness in a current of oxygen. Added to melted glass it imparts a purple color to it.

86. Red oxide of manganese, Mn_3O_4 , trimanganese tetroxide, is found crystallized in tetragonal pyramids as the mineral *hausmannite*. It is the most stable of the oxides and is formed when any of the others is heated in the air. It is a brown or reddish-brown powder having a specific gravity of 4.7, and resembles the corresponding lead oxide. It is probably a manganous manganic oxide having the formula $MnO \cdot Mn_2O_3$.

87. Manganese heptoxide, Mn_2O_7 , also known as *permanganic anhydride*, is a red, oily liquid prepared by the gradual addition of strong sulphuric acid to potassium permanganate, thus:



It is extremely unstable, decomposing with the evolution of oxygen together with the emission of violet fumes of the heptoxide, even at common temperatures. On heating, it decomposes violently. It absorbs moisture from the air, and is a powerful oxidizing agent, setting fire to most combustible bodies.

88. Manganous hydroxide, $Mn(OH)_2$, forms as a white precipitate when an alkali is added to a solution of a manganous salt out of contact with the air. It must be dried in a current of hydrogen, as it speedily oxidizes to Mn_2O_3 when exposed to the air. It occurs in nature as the mineral *pyrochroite*.

89. Manganic hydroxide, $MnO(OH)$, occurs in nature in steel-gray crystals as the mineral *manganite*. It gives a brown streak on unglazed porcelain and has a specific gravity of 4.3. It is formed when manganous hydroxide is allowed to stand in the air for a short time. Dilute nitric acid dissolves

part of it, forming manganous nitrate, the remainder being converted into the dioxide.

90. Manganous chloride, $MnCl_2$, is formed by dissolving any of the oxides or hydroxides, or the carbonate of manganese in hydrochloric acid, with the aid of heat. It is obtained in large quantities as a by-product in the preparation of chlorine for use in the manufacture of bleaching powder. When a solution containing the chloride is sufficiently concentrated, the chloride separates in pink crystals having the composition $MnCl_2 \cdot 4H_2O$. When heated, these crystals fuse to an oily liquid and in moist air at this temperature are decomposed into the oxide and hydrochloric acid.

If manganic hydroxide is dissolved in cold hydrochloric acid, a brown solution is obtained that is believed to contain manganese trichloride, $MnCl_3$. Similarly, if the dioxide is dissolved in cold hydrochloric acid, a brown solution is obtained that is thought to be manganese tetrachloride, $MnCl_4$. Neither of these compounds has been isolated, and if allowed to stand they gradually lose chlorine and become pink, when they contain $MnCl_2$. If heat is applied, this change takes place rapidly.

91. Manganous sulphate, $MnSO_4$, is prepared by dissolving manganous carbonate, $MnCO_3$, in sulphuric acid, or by heating a paste of manganese dioxide and sulphuric acid to redness and leaching with water. The properly concentrated rose-colored solution deposits between 0° and 6° C., oblique rhombic prisms, isomorphous with green vitriol and containing 7 molecules of water. Between 7° and 20° C., manganous sulphate crystallizes with 5 molecules of water, like cupric sulphate, with which it is then isomorphous. Between 20° and 30° C., it is deposited in oblique rhombic prisms that then contain only 4 molecules of water. All of these crystals are pink-colored, and their color is deeper the more water of crystallization they contain; all are extremely soluble in water.

92. Manganous sulphide, MnS , or *manganese monosulphide*, occurs in nature as the mineral *alabandite*, in steel-gray crystalline masses having a green streak. It is prepared

by heating one of the oxides of manganese, or manganese carbonate in a current of hydrogen sulphide. It is obtained in this way as a dark powder, but when heated to a high temperature it melts and forms a steel-gray crystalline mass. Alkaline sulphides precipitate manganous sulphide from solutions of manganous salts as a flesh-colored precipitate that turns brown on exposure to the air. When the flesh-colored precipitate is boiled with an excess of alkaline sulphide it changes into a green crystalline mass. Manganous sulphide unites with the alkaline sulphides, forming salts, and is soluble in hydrochloric acid.

The *disulphide*, MnS_2 , occurs as *hauerite*, has a metallic luster, and a reddish-brown color.

93. Manganic acid, H_2MnO_4 , has not been obtained, but salts of the acid, *manganates*, isomorphous with the sulphates and chromates, are known. The manganates are green in color, and their solutions are unstable except in the presence of considerable free alkali. Treated with carbon dioxide or made slightly acid, they are converted into the corresponding permanganate. In an alkaline solution the manganates are powerful oxidizing agents.

94. Potassium manganate, K_2MnO_4 , is prepared by fusing a mixture of manganese dioxide and caustic potash, thus:



In the presence of an oxidizing agent the sesquioxide is converted into the manganate.

Potassium manganate is a green-colored mass soluble in water.

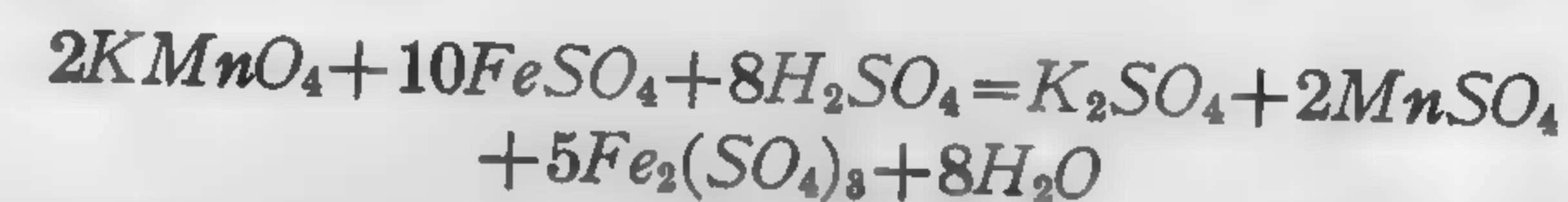
95. Sodium manganate, Na_2MnO_4 , is formed in the same manner as the potassium salt, and crystallizes with 10 molecules of water, soluble in water, with partial decomposition. This solution is used as a deodorizer and is used for disinfecting purposes under the name of *Condy's green disinfecting fluid*.

96. Permanganic acid, $HMnO_4$, is prepared by the addition of sulphuric acid to barium permanganate, or by the

electrolysis of potassium permanganate. It is a deep-red liquid having a bitter metallic taste, and readily decomposes under the action of light or heat.

97. Potassium permanganate, $KMnO_4$, is prepared by heating to dull redness a mixture of manganese dioxide, potassium hydroxide, and potassium chlorate. The dark-green mass obtained is leached with boiling water, and the solution is filtered and allowed to crystallize. The crystals are dark violet, almost black prisms, with a steel-blue metallic luster, have a sweet taste, with an astringent after taste. They have a specific gravity of 2.7, are soluble in 16 parts of water, forming a deep purple-colored solution, and decompose at $240^\circ C$.

Potassium permanganate is a powerful oxidizing agent, its solution being bleached by substances such as ferrous salts, etc., these substances being raised to a higher valence in the process. Thus, the action of ferrous sulphate on potassium permanganate breaks the permanganate up into potassium sulphate and manganese sulphate, while the ferrous sulphate is oxidized to ferric sulphate, according to the following equation:



Organic substances, especially the offensive emanations from putrescent organic matter, are readily oxidized by potassium permanganate. It is extensively used under the name of *Condy's red disinfecting fluid*.

98. Sodium permanganate, $NaMnO_4$, is prepared in a similar manner to the potassium salt. It is distinguished from the latter by its being deliquescent. Being cheaper than potassium permanganate, it is frequently used in place of the more expensive salt.

INORGANIC CHEMISTRY

(PART 11)

FAMILY 8, SERIES 3

GENERAL REMARKS

1. The part of Series 3 falling in Family 8 consists of the three similar metals *iron*, *cobalt*, and *nickel*. These follow after chromium and manganese in the third series and in some respects resemble those elements. Iron, like manganese, forms two series of salts—the ferrous salts, in which it appears to be divalent; and the ferric salts, in which it appears to be trivalent. The ferric compounds seem to be the more stable; the ferrous compounds when allowed to stand are usually changed to the ferric condition by the oxidizing action of the air. Iron also resembles chromium and manganese by forming ferric acid, which is analogous in composition to chromic and manganic acids. Cobalt and nickel resemble iron by forming two series of salts corresponding to the two series formed by iron; but their tendency to form salts in which the metals act as bivalent elements is much stronger than is their tendency to form salts in which they appear to be trivalent. The salts of trivalent nickel are very few. There is considerable difference of opinion as to whether the compounds of iron should be written with the single or double formula. That is, for instance, whether ferrous and ferric chlorides should be written $FeCl_2$ and $FeCl_3$ or Fe_2Cl_4 and Fe_2Cl_6 , respectively. In the case of ferric chloride there seems to be some evidence

in favor of the double molecule, but it is by no means conclusive, and as there is no definite evidence it is just as well to use the simpler formula, as this is what probably takes part in the reactions at all events. The same applies to cobalt and nickel.

IRON

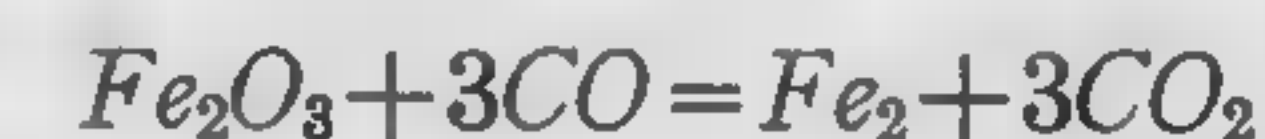
Symbol *Fe*. Atomic weight 55.84. Valence II, III, and VI(?).

2. History and Occurrence.—Iron is one of the most useful metals and at the same time one of the most widely and abundantly diffused in nature. It has been known from the earliest historic times—Tubal Cain being an artificer in it. As found on the earth's surface, native iron generally contains nickel and is of meteoric origin. It occurs in plants and vegetables, and is an essential constituent of the animal body. Among the more important minerals in which it is found may be mentioned *hematite*, Fe_2O_3 ; *magnetite*, Fe_3O_4 ; *limonite*, or *brown hematite*, $2Fe_2O_3 \cdot 3H_2O$, or $Fe_4O_3(OH)_6$; *siderite*, $FeCO_3$; *pyrite*, FeS_2 ; and *pyrrhotite*, Fe_7S_8 . It also occurs in many silicates, to which it usually imparts a red color. Of these, hematite, magnetite, limonite, and siderite are used as ores.

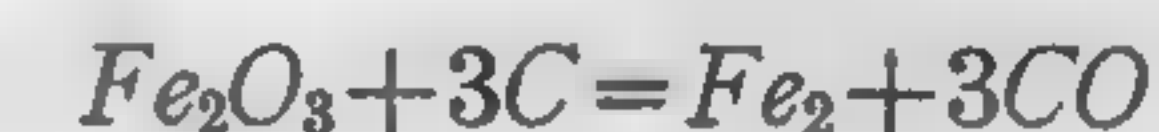
These ores are frequently associated with extraneous minerals that injure the quality of the iron. It is worthy of notice that scarcely one of these ores is entirely free from sulphur and phosphorus, substances that not only have a serious effect on the quality of the iron extracted from those ores, but also, by their presence in the iron, increase the difficulty of obtaining it in a marketable condition.

3. Preparation and Properties.—In the arts, iron is obtained on a large scale, either from the natural oxide, carbonate, or hydrated oxide. The ore, fuel, and limestone are placed in a *blast furnace*, which is from 40 to 100 feet high, and is shaped on the interior like a double cone. A powerful blast of hot air enters at the bottom, and the combustible matter, at the high temperature thus produced, removes the

oxygen from the ore, reducing it to the metallic state. The principal reducing agent is carbon monoxide, in which case the reaction may be written:



But the reduction is also partially accomplished by means of the carbon of the fuel, in which case the reaction may be represented by the equation:



The limestone unites with the silica and other impurities present, forming a fusible silicate that collects above the melted iron and is drawn off as *cinder* or *slag*. After the iron is reduced to the metallic state, it takes up more carbon, becomes fusible, melts, and runs down to the bottom of the furnace, which is called the *crucible*, or *hearth*. When enough has collected, it is tapped by drilling through the clay plug that closes the opening and the melted iron runs down a suitable channel into molds made in the sand for its reception. The manufacture of cast iron in the blast furnace is a continuous operation; the materials are constantly added above, and the cinder and melted iron are drawn off from below generally about five times a day, until the furnace needs repairs, or until other reasons put a temporary stop to further manufacturing. The frequency with which the iron, as well as the cinder, is drawn off varies in different places and under different conditions; it depends largely on the rapidity with which the iron is being produced.

4. Pig Iron.—The iron thus obtained is known in the market as *cast*, or *pig iron*; three varieties of it are known, namely, *white pig iron*, which is formed when the furnace is heavily charged or is working at a low temperature; it is hard, brittle, and crystalline, uniformly brilliant and white, of specific gravity 7.5, and readily fusible, but does not become very liquid; *gray pig iron* is formed at high temperatures, is granular in structure, of a gray color, very soft, difficultly fusible, but is quite liquid when melted, and has a specific gravity of 7.1; and *mottled pig iron*, which has intermediate properties.

The gray iron has, as a rule, the least combined carbon, its color being due to a separation of a part of this carbon as graphite during the cooling. Hence, the same metal suddenly cooled, as when chilled or cast in iron molds, may be hard and white; and when cooled slowly in sand, be soft and gray. White iron, and especially an alloy of iron and manganese known as *spiegeleisen*, contains a relatively high percentage of carbon; gray iron contains considerably less.

Iron is refined, or converted into *wrought iron*, by burning out the carbon and silicon, as well as the sulphur and phosphorus; this is effected usually by the process of *puddling*, or *boiling*. The pig iron is piled up on the floor of a reverberatory furnace, in contact with some of the pure ores. On lighting the fire it melts, and is then continually stirred to mix it thoroughly with the oxide. The carbon and silicon are gradually oxidized, the former escaping as gaseous monoxide and the latter being retained as silicate of iron in the slag, until finally the iron becomes pasty and clings together in spongy masses. These are collected into balls, and compacted, first, by working between powerful jaws, called *squeezers*, and then between rolls, by which the slag is pressed out, and the iron is made into *muck bars*. The puddled bar is cut into short pieces, made into bundles, heated, and again passed through the rolls; this operation is repeated until the wrought iron is sufficiently pure. By this process the carbon is reduced to one-half of 1 per cent., sometimes to even less, and the other foreign matters to mere traces. If the iron retains phosphorus, it is brittle when cold, and is called *cold-short*; if it retains sulphur, it is brittle when hot, or *red-short*. The iron thus obtained is bluish gray in color, is fibrous in structure, and has a specific gravity of 7.3 to 7.9.

Pure iron may be prepared from the best commercial varieties, pianoforte wire for instance, by fusing them with pure iron oxide, beneath a layer of glass to keep out the air, in a clay crucible. It is brilliant silver white in color, softer than wrought iron, capable of receiving a high polish, strongly magnetic, of specific gravity 7.8, and crystallizes in the regular system. Iron is also prepared for pharmaceutical purposes

by reducing its oxide by hydrogen at a red heat. It is then obtained as a black powder, which burns when heated in the air. In its purest commercial form, iron has a greater tenacity than any other metal, except nickel and cobalt. Its ductility is also very great, and when heated it may be rolled into sheets scarcely thicker than paper. At a full red heat it becomes pasty like wax, and may then be welded. It melts at a temperature of about $1,553^{\circ}\text{C}$., whereas cast iron melts at $1,100^{\circ}$ to $1,300^{\circ}\text{C}$., wrought iron $1,800^{\circ}$ to $2,200^{\circ}\text{C}$., and steel from $1,300^{\circ}$ to $1,600^{\circ}\text{C}$.

5. Steel, according to the American usage of the term, is iron that has been treated by one of several processes. The products included under this name contain from less than .1 to

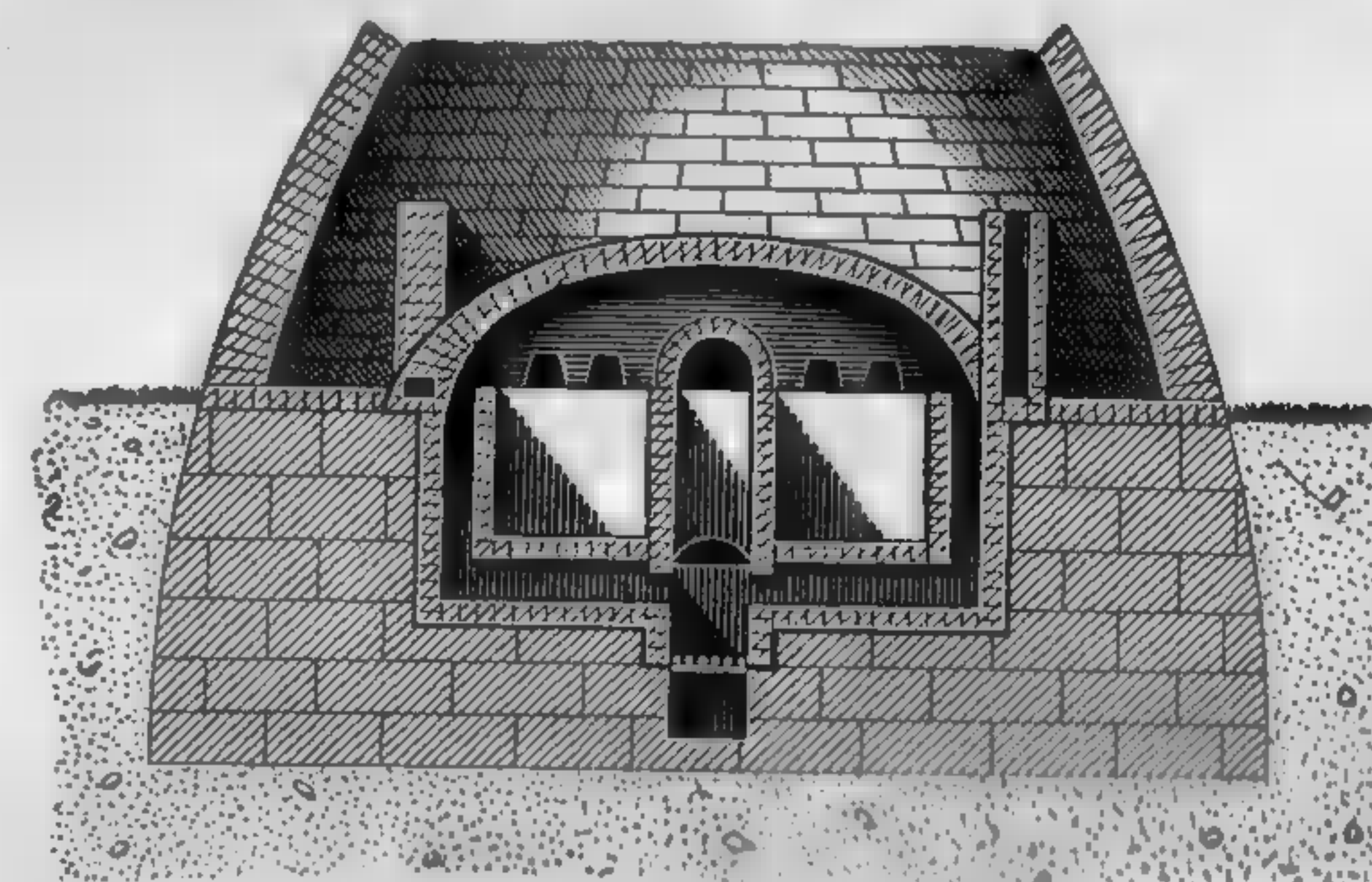


FIG. 1

more than 1.5 per cent. of carbon, and possess nearly all the chemical and physical properties, except those peculiar to cast iron, which belong to the commercial forms of this metal. Several methods may be employed for producing steel, but only three of these are of commercial importance at the present time, in this country at least. These are known as the *Bessemer*, the *open-hearth*, and the *crucible processes*.

1. A process that was formerly used almost exclusively, but has been almost entirely superseded, consisted in heating the wrought-iron bars, and thus causing them to take up a portion of the carbon. This is known as the *process of cementation*. Fig. 1 represents a cross-section of the furnace in which it is effected. The iron bars are packed in charcoal in the

fireclay chests, or boxes, shown in the figure, the whole covered with sand to exclude the air, and heated to redness for from 7 to 10 days, after which it is allowed to cool down slowly. The bars are now brittle, covered with blisters, and are easily fusible. They may be at once piled together, heated, and rolled into bars of *shear steel*, or they may be broken into small pieces, melted in crucibles of fireclay, with the addition of a little manganese dioxide, and cast into ingots; these ingots are afterwards drawn out under the hammer into bars. In this form it is known as *cast steel*.

2. The *Bessemer process* derived its name from its inventor, Henry Bessemer. The molten pig iron is run into a large egg-shaped vessel, called the *converter*, Fig. 2. This is made of iron plates bolted together and lined with ganister (a fairly

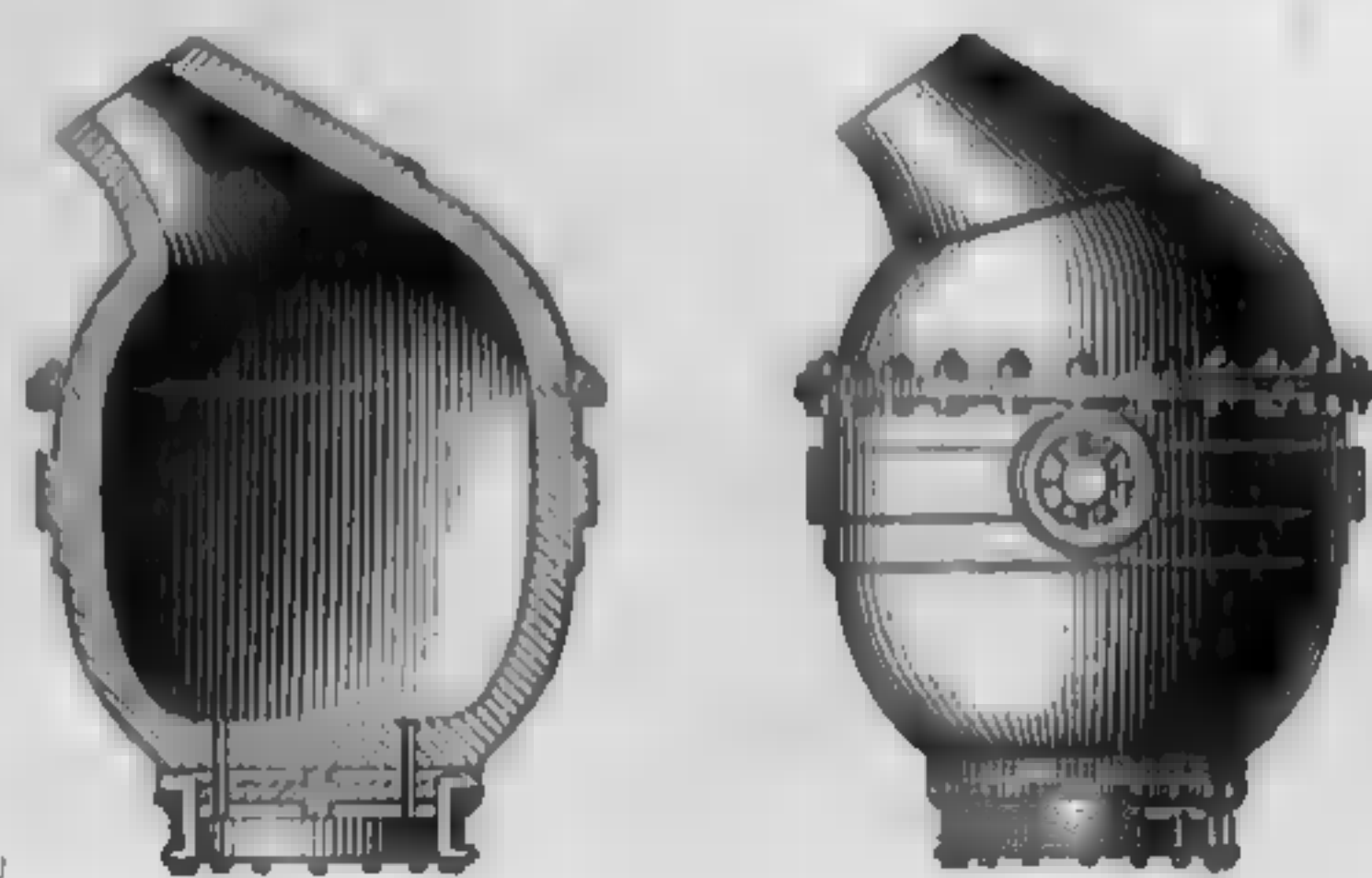


FIG. 2

pure sand). The bottom, which is interchangeable, contains a number of small openings or tuyères about $\frac{1}{4}$ to $\frac{1}{2}$ inch in diameter, through which air is blown at a pressure of about 25 pounds per square inch. The converter is turned into a horizontal position

to receive the charge of from 5 to 20 tons, which has previously been melted in a cupola, and it is then replaced in a vertical position, while at the same time a moderate blast of air is sent through the tuyères. This blast is merely to prevent the liquid iron from running into the tuyères. The silicon, manganese, carbon, and a portion of the iron burn in the stream of air, producing a very high temperature, which serves to keep the iron in a molten condition. The carbon is converted into carbon monoxide, which burns with a long flame at the mouth of the converter and is usually accompanied by a stream of sparks from the combustion of the iron. The blow is continued until the flame of carbon monoxide disappears. If continued longer the combustion proceeds at the expense of the iron. The blast is then lowered in pressure and the necessary amount of spiegeleisen or ferromanganese added

and the blast turned on again for a few minutes, after which the molten steel is run into ingot molds by tilting the converter. This process, as described, requires an iron free from sulphur and phosphorus. If, however, the converter is lined with a basic material, as done by Gilchrist and Thomas, using a calcined dolomite, pig iron containing varying amounts of phosphorus can be used.

3. In the *open-hearth process* a reverberatory furnace built over regenerating flues is used. These flues are heated by the waste gases from the furnace and in turn heat the gas and air passing to the hearth of the furnace. Two forms of this process are in use, namely, the *acid*, requiring a hearth made of infusible silicious material, and the *basic*, using a hearth made of *dolomite*. The latter process is the one most generally used, as pig iron can be converted directly with this modification.

The charge of pig iron, scrap iron, steel, and limestone is melted on the hearth of the furnace by a flame of carbon monoxide raised to a high temperature by the regenerators. When the charge has melted, iron ore, generally hematite, and some limestone are added. A violent boiling now ensues and slag is formed by the silica, obtained by the oxidation of the silicon present, combining with the ferrous oxide of the ore. The carbon is next removed by oxidizing it to carbon monoxide, and the phosphorus goes into the slag. A test piece of steel is withdrawn and the end of the process determined by the fracture and analysis of this test. When the process is complete the steel is run into a ladle when ferromanganese is added if required to deoxidize and recarbonize, and then the steel is run into ingots.

Liquid metal direct from the blast furnaces is sometimes used in place of pig iron.

6. **Properties of Steel.**—As steel is a term applied to a variety of material, produced by various processes, and differing in chemical composition, its properties cannot be definitely stated, but differ with the different varieties. The so-called *mild steel*, which contains a low percentage of carbon, is relatively soft and malleable and probably cannot be hardened

by any physical treatment. On the other hand, steel that contains more carbon, if heated to a rather high temperature and suddenly cooled, or "quenched," by dipping it in cold water, becomes very hard. A steel containing a high percentage of carbon becomes much harder when treated in this way than one containing a smaller quantity of this element, and those samples containing but mere traces of carbon, as stated before, cannot be hardened to any considerable extent by this process. It thus appears that the property of hardening when suddenly cooled from a high temperature depends largely, if not entirely, on the carbon content of the steel. Careful study and examination of steel under varying conditions have led to the belief that the phenomena attending the hardening and softening of steel by changes of temperature, are due to the forms assumed by the carbon under varying conditions.

Osmond holds that there are two allotropic forms of iron, which he calls α and β iron, and that the changes produced by variations in temperature are due to the conversion from one to the other of these forms. This theory, however, is not required to account for the changes observed and is not generally accepted. If a piece of high-carbon steel is heated to a high temperature and quenched, it becomes exceedingly hard—too hard, in fact, for ordinary purposes. If this is again heated to the same temperature and cooled slowly, it loses its hardness, and assumes the properties it possessed before heating; but if instead of heating to the high temperature used in hardening, it is heated to a much lower temperature and cooled, suddenly as a rule, though not always, its hardness is modified or *tempered*, but not destroyed. It should be noted that the word tempering is frequently, and not altogether incorrectly, applied to any heating and sudden cooling of iron.

When the hardened steel is reheated, a thin film of oxide is formed on its surface, imparting different colors to the metal, by which its temperature can be judged with considerable accuracy. In Table I, which is compiled from the most reliable sources, the temperature to which steel is heated in tempering it for various instruments is given, together with the color assumed in each case.

7. Manganese, nickel, vanadium, chromium tungsten, and molybdenum appear to make steel hard in whatever manner it is cooled. Without being heated treated, however, these alloy steels are only slightly superior to plain carbon steels. Manganese steel is very tough and is used when long-continued wear is essential, in the jaws of crushing machines, elevator buckets, etc. Nickel is added to increase the strength and is used chiefly for armor plate, forgings, and castings. It does not affect the ductility of the steel. Vanadium acts in a similar manner to nickel, but less vanadium is required to obtain the same effect. Chromium is used to increase the

TABLE I
TEMPERING OF STEEL

Temperature Degrees C.	Color	Implements Tempered
230	Pale straw yellow	Surgical instruments, razors, metal engraving tools
243	Straw yellow	Knives, hammers, metal shears, steel cold chisels
254	Brown	Hatchets, scissors, rock and hard-coal drills
266	Brown-purple	Axes, planes, picks
277	Purple	Wood-turning tools, soft-coal picks, and drills
288	Bright blue	Springs, augers
293	Full blue	Soft-iron cold chisels
316	Dark blue	Spiral springs, hand and power saws

hardness of surfaces and to resist severe shocks. Tungsten tends to harden the steel and to prevent softening due to increase of temperature. Steels containing tungsten are frequently known as self-hardening steels, and are used for high-speed lathe, planing, and boring-mill tools. Molybdenum steels possess properties similar to those of tungsten steels, but they are tougher than the latter. Molybdenum steels are used for some high-grade saws. There are also many alloy steels which contain more than one of these elements.

OXIDES OF IRON

8. Three oxides of iron are known, namely: ferrous oxide, FeO ; ferric oxide, Fe_2O_3 ; ferrous-ferric oxide, Fe_3O_4 .

9. **Ferrous oxide**, FeO , may be obtained as a black powder by igniting ferrous oxalate in a closed vessel. **Ferrous hydroxide**, $Fe(OH)_2$, is formed as a white precipitate when an alkaline hydroxide is added to the solution of a ferrous salt. White flocks are thus produced, which, dried away from the air, have a slightly greenish tint, but which, on exposure, take fire and burn to ferric oxide. Ferrous oxide has a strong reducing action.

10. **Ferric oxide**, Fe_2O_3 , which occurs abundantly in nature, is called *hematite*, and is one of the most important of the iron ores. Artificially it may be prepared by igniting the hydroxide or by calcining ferrous sulphate. This salt first loses its water, and then at red heat decomposes into sulphur trioxide, sulphur dioxide, and ferric oxide:



A red powder is thus obtained, which is known in commerce under the name of *colcothar*, *rouge*, and *Venetian red*, and is used for polishing metals, glass, etc. Its specific gravity is 5.2. It is reduced to the metallic state when heated in hydrogen.

11. **Ferric hydroxide**, $Fe(OH)_3$, is prepared by adding ammonium hydroxide to the solution of a ferric salt, when it separates as a brownish-red precipitate, which may be washed and dried at a moderate temperature without decomposing. If, however, it is heated to $100^\circ C.$, or if the solution containing it is boiled for some time, it gradually loses water, forming the hydroxides $FeOOH$, $Fe_2O(OH)_4$, etc. When strongly ignited, these give up more water and are converted into ferric oxide. The hydroxide $FeOOH$ corresponds to the compounds $AlOOH$ and $CrOOH$, and is believed to form some salts.

12. **Ferrous-ferric oxide**, Fe_3O_4 , is found in nature as the mineral *magnetite*, and is believed to be the ferrous salt

of the hydroxide $FeOOH$. Its formula is therefore thought to be $Fe \begin{smallmatrix} O-Fe=O \\ O-Fe=O \end{smallmatrix}$. Franklinite is thought to resemble

this in composition and to be essentially $Zn \begin{smallmatrix} O-Fe=O \\ O-Fe=O \end{smallmatrix}$ in which some of the zinc is replaced by ferrous iron and manganese, or possibly a magnetite in which part of the ferrous iron is replaced by zinc and manganese. Ferrous-ferric oxide is formed when iron is burned in oxygen, or when steam is passed over red-hot iron.

The very stable character of Fe_3O_4 has permitted its application for protecting iron from rust. When superheated steam is passed over the red-hot metal, a very dense, strongly adhering film of Fe_3O_4 is produced, which effectually protects the metal (*Barff's process*). A similar coating is produced by the action of a mixture of air and carbon dioxide (*Bower's process*).

13. **Ferric acid**, H_2FeO_4 , while not known in the free state, forms ferrates, some of which are fairly well known. A solution of the potassium salt is formed when iron filings and potassium nitrate are strongly ignited, and the fused mass is extracted with water. The solution has a fine purple color. It can be prepared also by passing chlorine through a strong solution of caustic potash containing freshly precipitated ferric hydroxide in suspension. Potassium ferrate forms a black precipitate, insoluble in alkaline solutions, but soluble in water. It is very unstable. The solution decomposes on boiling with an evolution of oxygen, and precipitation of ferric hydroxide.

The ferrate of barium is prepared by adding barium chloride to a solution of either potassium or sodium ferrate. It is a dark-red powder, soluble in acetic acid, and fairly stable.

14. **Ferrous carbonate**, $FeCO_3$, occurs in nature as *siderite*, or *spathic iron ore*, in obtuse rhombohedrons, light grayish or yellowish in color, and of specific gravity 3.8. It is thrown down, on the addition of a soluble carbonate to a solution of a ferrous salt, as a white precipitate, rapidly passing into brown ferric hydroxide. It is soluble in water containing carbonic acid and is found in this state in nature in the waters of chalybeate springs.

SULPHIDES OF IRON

15. Iron disulphide, FeS_2 , being widely diffused, as *iron pyrites*, is the most important of the sulphides of iron. It occurs in nature in two distinct forms: one, brass-yellow and isometric, is known as *pyrite*; and the other, white or dull greenish-yellow and orthorhombic, is called *marcasite*. This latter variety can be altered much more readily than the other, and possesses a great tendency to attract oxygen from the air and become converted into *sulphate*. When heated in closed vessels, pyrite loses a part of its sulphur. Iron disulphide may be obtained artificially by heating iron with excess of sulphur to a temperature below redness, or by heating ferric oxide or hydroxide moderately in a stream of H_2S as long as it increases in weight.

16. Ferrous sulphide, FeS , is found in small quantities in many meteorites. It may be produced by the direct union of iron and sulphur, as when iron wire burns in sulphur vapor, or when the two substances are melted together in suitable proportions. It is a grayish-yellow solid with a metallic luster and crystalline structure, and is easily fusible. When finely divided, it is oxidized to ferrous sulphate on exposure to the air. With acids it evolves hydrogen-sulphide gas. It is precipitated from ferrous solutions by alkaline sulphides.

17. Ferric sulphide, Fe_2S_3 , may be prepared by heating iron and sulphur mixed in the proper proportions. It is not commercially important, and is interesting, theoretically, principally because it is analogous to Fe_2O_3 . Just as the hydroxide $FeOOH$, corresponding to the oxide Fe_2O_3 , forms salts, so does the hydrosulphide $FeSSH$.

CHLORIDES OF IRON

18. Ferrous Chloride.—When hydrochloric-acid gas is passed over iron filings heated to redness, **ferrous chloride, $FeCl_2$,** is obtained in white, shining, hexagonal scales that have a specific gravity of 2.5 and are deliquescent in moist

air. It is soluble in 2 parts of water, and the solution, evaporated and cooled away from the air, deposits crystals having the composition $FeCl_2 \cdot 4H_2O$. When heated in the air to drive off the water, these crystals decompose. Ferrous chloride may be prepared in solution by dissolving iron in hydrochloric acid, away from air. If the solution containing hydrochloric acid is exposed to air, the chloride will be oxidized to ferric chloride; but if the solution does not contain hydrochloric acid, it breaks up into ferric chloride, which remains in solution, and a basic chloride, which separates as a precipitate. Ferrous chloride unites with the chlorides of the alkalis, forming double chlorides of the composition K_2FeCl_4 , Na_2FeCl_4 , etc.

19. Ferric chloride, $FeCl_3$, is most readily prepared in solution by dissolving iron in hydrochloric acid, and saturating the solution with chlorine. This solution, especially if dilute, is decomposed into hydrochloric acid and an insoluble oxychloride when strongly heated. By treating the solution carefully, yellow crystals of $FeCl_3 \cdot 6H_2O$ may be obtained. These are decomposed into ferric oxide and hydrochloric acid if heated to drive off the water. The anhydrous chloride is obtained by heating iron in chlorine.

SULPHATES OF IRON

20. Ferrous sulphate, $FeSO_4$, long known under the names of *copperas* and *green vitriol*, is prepared by dissolving iron wire in dilute sulphuric acid. It is obtained as a by-product in the manufacture of copper sulphate, and by the decomposition of pyrite or marcasite. The pyrite is exposed to the weather by which it is oxidized.

Ferrous sulphate crystallizes in fine, green, monoclinic crystals, having the composition $FeSO_4 \cdot 7H_2O$, and a specific gravity of 1.9.

Ferrous sulphate dissolves readily in water and forms a pale-green solution. If this solution is heated, and on long standing, it decomposes, forming a muddy solution, due to the oxidation of the sulphate and the formation of a basic sulphate. Ferrous sulphate readily absorbs oxygen and, hence, is frequently used

as a reducing agent. In this capacity it is frequently used to precipitate gold in the metallic state from its solutions. Its principal use, however, is for the preparation of iron mordants for the dyeing industries, inks, Prussian blue, tanning, etc.

21. Ferric sulphate, $Fe_2(SO_4)_3$, is obtained by treating a solution of ferrous sulphate, containing sulphuric acid, with an oxidizing agent, or by dissolving ferric hydroxide in sulphuric acid, and evaporating the solution. It is a slightly yellowish mass that dissolves completely, though rather slowly, in water. The solution is yellow-brown, and has an acid reaction. When concentrated by evaporation, it deposits a deliquescent, yellowish, crystalline mass of hydrated ferric sulphate.

Ferric sulphate unites with sulphates of the alkalies, forming double sulphates that are analogous to alum, and are known as *iron alums*. The potassium salt has the composition $KFe(SO_4)_2 \cdot 12H_2O$.

22. Iron Phosphates.—*Ferrous phosphate, $Fe_3(PO_4)_2$,* occurs in nature with 8 molecules of water of crystallization, as the mineral vivianite. It may be precipitated from a ferrous solution by adding sodium phosphate.

Ferric phosphate, $FePO_4$, separates as a precipitate when sodium phosphate is added to a ferric solution.

COBALT

Symbol Co. Atomic weight 58.97. Valence II and III.

23. History and Occurrence.—The property, which certain cobalt compounds possess, of coloring glass blue was known to the ancients. The ores were long known to the German miners under the name of *cobalt*, a name derived from *kobold*, meaning an evil spirit, who, as they supposed, offered them an ore rich in appearance, but otherwise worthless. Brandt, in 1735, prepared the metal and his observations on its properties were confirmed by Bergman in 1780.

Cobalt does not occur free in nature except in meteoric iron. It usually occurs as *linnæite, $(CoNiFe)_3S_4$* ; *speiss cobalt*,

$CoNiFeAs_2$; *skutterudite, $CoAs_3$* ; *smaltite, $CoAs_2$* ; and *cobaltite, $CoAs_2 \cdot CoS_2$* .

24. Preparation and Properties.—Cobalt ores containing sulphur and arsenic are roasted and the roasted ores fused with lime or sand. The iron in the ore enters the slag, and the cobalt, in the form of speiss, sinks. The speiss is dissolved in hydrochloric acid, when any arsenate of iron is precipitated by means of bleaching powder and calcium hydrate. The clear supernatant liquid is drawn off and the heavy metals, copper, bismuth, etc., precipitated with hydrogen sulphide. Bleaching powder is added to the clear liquid remaining and the cobalt is precipitated as an oxide.

Metallic cobalt is prepared by igniting the oxide or the chloride in a current of hydrogen; by the electrolysis of the chloride; or by ignition of the chloride with sodium or potassium. It can be prepared also by heating the oxalate under powdered glass.

Cobalt is a silver-white metal, slightly tinged with red. It is harder than either iron or nickel, is malleable, and very ductile, and is magnetic. It melts at $1,530^\circ C.$, has a granular fracture and a specific gravity of 8.9. The compact metal does not change at the ordinary temperature, but the powder oxidizes very readily in the air. It is only slowly soluble in sulphuric and hydrochloric acids, evolving hydrogen, but is readily soluble in nitric acid.

COMPOUNDS OF COBALT

25. Cobalt forms three oxides: *cobaltous oxide, CoO* ; *cobaltic oxide, Co_2O_3* ; and *cobaltous-cobaltic oxide, Co_3O_4* .

26. *Cobaltous oxide, CoO ,* is obtained when one of the higher oxides is heated in a current of hydrogen or of carbon dioxide. It is prepared also by heating cobaltous hydroxide in the absence of air. It is a decidedly basic oxide, is a light-brown powder unaffected by the air at ordinary temperatures, and dissolves in acids, forming cobaltous salts. Heated in the air, it forms cobaltous-cobaltic oxide.

27. *Cobaltic oxide, Co_2O_3 ,* is obtained as a black powder when the nitrate is gently heated. It acts as a feeble base and

is soluble in acids, when it forms the cobaltic salts, which are unstable. When heated it yields the cobaltous-cobaltic oxide.

28. Cobaltous-cobaltic oxide, Co_3O_4 , is formed when any of the oxides or the nitrate is ignited in the air. It is a black powder, is used for the preparation of cobalt products and for painting on porcelain. Boiled with hydrochloric acid, it forms cobaltous chloride and evolves chlorine. It is analogous to Fe_3O_4 and is believed to have the composition represented by the formula $Co \begin{smallmatrix} O-Co=O \\ O-Co=O \end{smallmatrix}$.

29. Cobaltous hydroxide, $Co(OH)_2$, is the precipitate obtained when potassium hydroxide is added in excess to a solution of a cobaltous salt and boiling. A blue precipitate of a basic salt is first obtained, and this, on boiling, becomes converted into the rose-red hydroxide. This readily absorbs oxygen from the air, changing to the brown cobaltic hydroxide. *Cobaltic hydroxide, $Co(OH)_3$,* is obtained as a brownish black precipitate when an alkaline hypochlorite solution is added to a solution of a cobalt salt.

30. Cobaltous nitrate, $Co(NO_3)_2 \cdot 6H_2O$, can be prepared by dissolving cobaltous oxide in nitric acid. It forms red, deliquescent crystals that are easily soluble in water and melt somewhat under $100^\circ C.$, changing from red to blue when the water of crystallization has been expelled. On further heating, it is converted into cobaltic oxide. It is largely used as a blowpipe reagent.

31. When a solution of cobaltous nitrate is acidified with acetic acid and a solution of potassium nitrite is added, a yellow precipitate of **potassium-cobaltic nitrite**, or *cobalt yellow*, $K_3Co_2(NO_2)_{12}$, is obtained. It forms a yellow microcrystalline powder slightly soluble in water.

32. Cobaltous chloride, $CoCl_2$, is prepared by heating the powdered metal in chlorine gas, or by dissolving one of the oxides or the carbonate in hydrochloric acid. It crystallizes in red prisms with 6 molecules of water. Heated to $120^\circ C.$, these crystals change to the blue of the anhydrous salt. A

solution of cobaltous chloride forms the so-called *sympathetic ink*, for characters written with its pink solution are almost invisible until exposed to heat, when they become blue, and on exposure to the air gradually resume their original pink color.

33. By adding ammonium sulphide to a solution of a cobalt salt, a black precipitate of **cobaltous sulphide, CoS ,** is obtained. It differs from ferrous sulphide in being insoluble in dilute hydrochloric acid.

34. Cobaltous sulphate, $CoSO_4 \cdot 7H_2O$, occurs native as the mineral *bieberite*. It is prepared by dissolving the oxides or the carbonate in sulphuric acid. It crystallizes in red prisms isomorphous with ferrous sulphate, is not affected by the air, is soluble in water, has a weak, astringent, metallic taste, and is insoluble in alcohol. It is used for the manufacture of cobalt salts, and in decorating porcelain. It does not acquire a blue color when dried, and can be submitted to a high temperature without undergoing decomposition.

35. Cobaltous arsenate, $Co_3(AsO_4)_2$, occurs as *cobalt bloom* in violet needles containing 8 molecules of water of crystallization. It is soluble in dilute mineral acids. The **diarsenide, $CoAs_2$,** occurs as *smaltite*, or *speiss cobalt*, associated with iron and nickel.

NICKEL

Symbol Ni. Atomic weight 58.68. Valence II and III.

36. History and Occurrence.—Nickel was discovered by Cronstedt, in 1751, in a copper-colored mineral, to which, having failed in attempting to extract copper from it, the miners had applied in derision the name *kupfernickel*, and from which name nickel has been derived. Except in meteoric irons, nickel does not occur native, but is a constituent of many minerals. It occurs as *nichelite, $NiAs$* ; *gersdorffite, $NiSAs$* ; *ullmannite, $Ni_2S_2(AsSb)_2$* ; *annabergite, $Ni_3(AsO_4)_2 \cdot 8H_2O$* ; and *garnierite, $2(NiMg)_3Si_4O_{10} \cdot 3H_2O$* .

37. Preparation.—The sulphide ores containing nickel are first roasted to remove the excess of sulphur and to oxidize

the iron, after which the ore is smelted in a blast furnace. This produces a matte containing from 35 to 40 per cent. of nickel and copper. This matte is then concentrated to a matte containing 70 to 80 per cent. of nickel and copper, either in a blast furnace, or by means of a converter. The nickel is separated from the copper and the small amount of iron still remaining in the matte by fusion with sodium sulphate and coke in a magnesium lined, open-hearth reverberatory furnace. While in a molten condition in this furnace the charge is poled frequently for a matter of 5 hours. Sodium sulphide is formed and this dissolves the copper and iron sulphides, and the nickel sulphide is tapped into molds. The nickel sulphide is roasted with sodium nitrate, the oxide obtained is washed, dried, and pressed into cubes with powdered charcoal and strongly ignited in clay crucibles on the hearth of a reverberatory furnace. A furnace in which this reduction can be carried on continuously has been devised and is replacing the reverberatory furnace. This furnace has vertical tubes of fireclay passing through it. The tubes are charged at the top with the nickel oxide and charcoal and the metal is drawn off at the bottom.

Another method, known as the *gas method*, consists of exposing the roasted matte to the action of water gas or producer gas at a temperature of about 400° C. The reduced metal is then exposed to a current of carbon monoxide and forms nickel carbonyl, $Ni(CO)_4$. This is then passed through chambers heated to 180° C., in which the nickel is deposited.

38. Properties.—Nickel is a pure, silver-white metal having a hardness of about 3.5 and a specific gravity of 8.0. It is capable of taking a high polish and is malleable and ductile. It does not oxidize in dry or moist air at ordinary temperatures, melts at 1,450° C., and distills in the electric furnace. It is magnetic but loses its magnetism when heated.

Nickel is used for various industrial purposes. The steel and plating industries consume the most of the nickel produced. Small quantities are used in the manufacture of laboratory and cooking utensils. Alloys of nickel are used in coinage, jewelry, boiler and condenser tubes, and for scientific apparatus.

39. Nickel alloys with a great many metals and forms some very important and useful compounds. Among the most important are:

Aluminum nickel, which is composed of 28 to 30 per cent. of aluminum and from 40 to 72 per cent. of nickel, is used for cheap jewelry. Nickel slightly hardens and toughens aluminum.

Chrome nickel, which is used for making high-speed tool steel. It contains 73 per cent. of chromium, 23 per cent. of nickel, 2.5 per cent. of iron, 1 per cent. of carbon, and .5 per cent. of silicon.

Molybdenum nickel, which is also used to alloy with steel and usually contains 40 to 75 per cent. of molybdenum, 20 to 50 per cent. of nickel, 2 to 2.5 per cent. of iron, 1 to 1.5 per cent. of carbon, and from .25 to .5 per cent. of sulphur.

Invar, which is an alloy of iron and nickel containing 36 per cent. of nickel and 64 per cent. of iron, is used for the manufacture of measuring instruments. The valuable property of this alloy lies in the fact that it has no expansion when heated.

Above 36 per cent. of nickel, the nickel iron alloys are influenced by temperature, the coefficient of expansion increasing with the proportion of nickel.

Platinite, which is an iron-nickel alloy containing 42 per cent. of nickel, has the same coefficient of expansion as glass, and is used for making armored glass.

Ferro-nickel, which is an iron compound containing from 25 to 75 per cent. of nickel, is used to increase the elasticity and tenacity of steel. It is used in the manufacture of steel for armor plates, guns, etc.

Constantan, which is the trade name for an alloy used largely for the manufacture of resistance devices for electrical work. It contains 40 per cent. of nickel and 60 per cent. of copper.

German silver, which consists of 50 to 60 per cent. of copper, 20 to 30 per cent. of nickel, and from 20 to 30 per cent. of zinc, is a silvery-white compound used in the manufacture of jewelry, scientific instruments, resistance wires, etc.

Monel metal, which is an alloy of 3 parts of nickel to 1 part of copper, is obtained from the copper-nickel deposits of the Sudbury district. It has a silver-white color and takes a high

polish; it has a high melting point, great tensile strength, and resists corrosion, particularly by the strong acids.

Alloys of copper with nickel and zinc, or with nickel alone, are used in this country, Germany, Belgium, and Switzerland for the manufacture of small coins. The advantages of nickel coins are: (1) nickel being dearer than copper, the coins can be made smaller for the same value, and consequently they are more convenient to handle; (2) the alloy is hard and therefore wears well; and (3) its manufacture not only requires skilled workmen, but also powerful machines, facts that offer a certain safeguard against counterfeiting.

COMPOUNDS OF NICKEL

40. *Nickelous oxide*, NiO , and *nickelic oxide*, Ni_2O_3 , are known. **Nickelous oxide** is an ash-gray powder that is obtained by strongly igniting the nitrate or carbonate of nickel. On adding potassium hydroxide to a nickel salt, an apple-green precipitate of *nickelous hydroxide*, $Ni(OH)_2$, is formed. When heated this is converted into nickelous oxide.

Nickelic oxide, Ni_2O_3 , is a black powder prepared by the careful ignition at a low temperature of the nitrate or carbonate. *Nickelic hydroxide*, $Ni(OH)_3$, is precipitated as a black powder when the solution of a nickel salt is treated with sodium hypochlorite. As nickelic oxide and hydroxide are the only compounds in which nickel acts as a trivalent element, the endings *ous* and *ic* are seldom used in speaking of the other compounds of nickel.

41. **Nickel chloride**, $NiCl_2$, may be obtained anhydrous by the action of chlorine on nickel filings; it is volatile at a dull-red heat, and sublimes in golden-yellow scales. It may be obtained in solution by the action of boiling water on the anhydrous salt, or by the action of hydrochloric acid on either oxide or carbonate of nickel. Its solution is green, and after proper concentration deposits beautiful green crystals having the composition $NiCl_2 \cdot 6H_2O$.

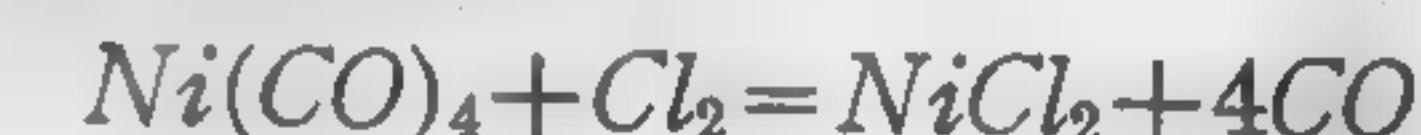
42. **Nickel sulphate**, $NiSO_4$, is deposited in fine emerald-green prisms, having 7 molecules of water, isomorphous

with magnesium sulphate, when its solution is allowed to evaporate spontaneously below $15^\circ C$. There is another sulphate containing 6 molecules of water that is dimorphous. When deposited between 20° and $30^\circ C$. it crystallizes in octahedrons, but when its solution is made to crystallize between 60° and $70^\circ C$., monoclinic crystals are obtained isomorphous with the corresponding sulphates of zinc and cobalt. Nickel sulphate dissolves in three times its weight of water at $10^\circ C$.

43. **Nickel ammonium sulphate**, $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$, is prepared by dissolving pure nickel in dilute sulphuric acid and adding ammonium sulphate to the solution. The crystalline paste formed is purified by recrystallization. It forms green, monoclinic prisms somewhat soluble in water. It is the salt used in nickelplating.

44. **Nickel sulphide**, NiS , is obtained as a black precipitate by the action of an alkaline sulphide on a salt of nickel; like cobalt sulphide, it is insoluble in HCl , but ammonium disulphide dissolves it to a dark-brown liquid.

45. **Nickel carbonyl**, $Ni(CO)_4$, is obtained when carbon monoxide is passed over metallic nickel at a temperature of from 350° to $400^\circ C$. It is a colorless liquid boiling at $43^\circ C$.; it solidifies at $-25^\circ C$. and forms needle-shaped crystals. It is soluble in alcohol, benzene, and chloroform, but is insoluble in dilute acids or alkalis. Its vapor decomposes at $150^\circ C$. into nickel and carbon monoxide. Chlorine decomposes it according to the equation:



and from this it is judged to have the composition shown by

the formula $Ni \begin{array}{c} \diagup CO-CO \\ | \\ \diagdown CO-CO \end{array}$. Its vapor is very poisonous.

46. **Nickel carbonate**, $NiCO_3$, is obtained as pale-green rhombohedra when a solution of nickel chloride is heated with calcium carbonate. When a solution of an alkaline carbonate is added to a solution of a nickel salt a pale-green precipitate of a basic nickel carbonate of varying composition is thrown down.

FAMILY 8, SERIES 5

47. The elements of Family 8 falling in Series 5 are *ruthenium*, *rhodium*, and *palladium*. Just as in Family 8, Series 3, iron forms the greater number of compounds and nickel the least number, so in this series ruthenium forms the highest number and palladium the lowest. There appears to be a gradual decrease in valence in each case. In nature these elements are usually associated with the elements of Family 8, Series 9, and frequently also with gold.

RUTHENIUM

Symbol Ru. Atomic weight 101.7. Valence II, IV, VI, and VIII.

48. Ruthenium was discovered by Osann, in 1828, in the platinum ores from the Ural. Very little was known regarding it until 1846, when Claus investigated the metal. He retained the name ruthenium which had been given to this metal by Osann. It occurs in platinum ores and as the sulphides of ruthenium and osmium in the mineral *laurite*. Ruthenium is prepared by igniting the residues left after extracting the platinum from its ores in a stream of chlorine in the presence of sodium chloride. The fused mass is dissolved in water, potassium nitrite is added, the solution neutralized with sodium carbonate, and evaporated to dryness. The double nitrites of ruthenium and potassium are extracted with absolute alcohol, leaving any rhodium present in the residue. After adding water to the solution and distilling off the alcohol, the solution is made acid with hydrochloric acid, when a red solution of the double chlorides are obtained. This is treated with sal ammoniac, forming ammonium-ruthenium chloride, after which the ruthenium is precipitated by mercuric chloride, crystallized and ignited when pure ruthenium is obtained.

49. Ruthenium is a hard, heavy, white, brittle metal with a specific gravity of 12.06. With the exception of osmium, it is the most difficultly fusible of the platinum metals. It can be melted in the electric arc and becomes malleable when hot. Ruthenium combines with chlorine at a red heat, is insoluble in acids, being scarcely attacked by even aqua regia.

COMPOUNDS OF RUTHENIUM

50. Three oxides of ruthenium are known. The *sesquioxide*, Ru_2O_3 , is obtained as a blue powder insoluble in acids by heating the finely divided metal in the air. When metallic ruthenium is fused in an oxidizing atmosphere or the sulphate is roasted in the air, the *dioxide*, RuO_2 , is obtained. It crystallizes in small pyramids, which are very hard, have a green, metallic luster, and a specific gravity of 7.2. The *peroxide*, RuO_4 , is formed when ruthenium is heated to $1,000^\circ C.$ in oxygen and is cooled rapidly, or by heating ruthenium with potassium nitrate and hydroxide and saturating the solution of the fused mass with chlorine. It is soluble in water, melts at $25.5^\circ C.$, and decomposes without explosion at $107^\circ C.$

Ruthenium trichloride, $RuCl_3$, is formed when the metal is heated in a mixture of chlorine and carbon dioxide. It forms orange-colored solutions, which, on treatment with hydrogen sulphide, are changed to blue solutions of the *dichloride*, $RuCl_2$. Double chlorides, known as *chlororuthenites*, M_2RuCl_5 , and *chlororuthenates*, M_2RuCl_6 , exist. Sulphates corresponding with RuO and Ru_2O_3 have also been obtained.

RHODIUM

Symbol Rh. Atomic weight 102.9. Valence II, III, and IV.

51. Rhodium was discovered by Wollaston, who announced his discovery in 1804. He gave it the name of rhodium, from the rose color of the solution of rhodium salts. The metal and compounds were investigated by Berzelius and Claus. It is found in platinum ores and with some rare gold ores.

Rhodium is prepared by treating the solution from which the platinum has been precipitated with metallic iron, which precipitates the metals still in solution. This precipitate is fused with lead, and the lead, copper, and palladium dissolved out with nitric acid. The residue is digested with nitric acid and chlorine, or with aqua regia, converting the rhodium into the chloride, which is precipitated as the double ammonium chloride, is purified by repeated recrystallization, and ignited in the oxyhydrogen flame.

52. Rhodium forms a hard, white metal of the color and luster of aluminum. It has a specific gravity of 12.1, is more difficult to melt than platinum, melting at about $2,000^{\circ}\text{C}$., and is nearly as ductile as silver. Rhodium is unaltered in the air at ordinary temperatures, but oxidizes at a red heat. When solidifying after melting it spits as does silver, the surface becoming blue from oxidization. It can be distilled at the temperature of the electric furnace. When the metal is precipitated from solutions of its salts by alcohol or formic acid, it is obtained as a spongy, black powder. Pure rhodium is practically insoluble in all the acids, singly or together. Alloyed with zinc, lead, or copper, it is soluble in aqua regia. This is also true of alloys of platinum and rhodium containing small amounts of rhodium. On the other hand it does not dissolve in aqua regia, when alloyed with gold or silver. Rhodium can be dissolved by repeatedly fusing it with potassium bisulphate or with acid phosphates. Chlorine readily attacks rhodium.

RHODIUM COMPOUNDS

53. Rhodium forms a *monoxide*, RhO ; a *dioxide*, RhO_2 ; and a *sesquioxide*, Rh_2O_3 . Only one chloride, the *trichloride*, RhCl_3 , is known. Rhodium burns in sulphur, forming the *monosulphide*, RhS ; a *sesquisulphide*, Rh_2S_3 , is obtained when hydrogen sulphide is passed over hot solutions of rhodium salts. A yellow crystalline *sulphate*, $\text{Rh}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, with a sour astringent taste is obtained when the hydrated hydroxide, having the formula $\text{Rh}(\text{OH})_3 \cdot \text{H}_2\text{O}$, is dissolved in sulphuric acid.

PALLADIUM

Symbol Pd. Atomic weight 106.7. Valence II and IV.

54. Palladium was discovered at the same time as rhodium by Wollaston. It occurs associated with platinum and alloyed with native gold. When alloyed with gold the palladium is obtained by fusing the alloy with silver, dissolving the silver and palladium in nitric acid, precipitating the silver with sodium chloride, and throwing the palladium out of solution with metallic zinc. Palladium is distinguished from platinum by its forming an insoluble cyanide. This fact is frequently taken advantage of in the preparation of the metal. Mercuric cyanide is added to a solution containing palladium, precipitating the cyanide, which is then ignited and yields spongy palladium.

55. Palladium is a hard, silver-white metal having a specific gravity of 11.4, and melting at $1,541^{\circ}\text{C}$. It is malleable and ductile. When heated to a dark red it assumes a green to violet tint. It is only slightly tarnished in the air, but at a red heat it becomes coated with a coating of the oxide. It is slowly soluble in nitric acid.

Palladium is remarkable for its power of absorbing hydrogen in large quantities (occlusion). It occludes hydrogen even at ordinary temperature, but if heated to 100°C . in hydrogen it takes up over 960 times its own volume of the gas, and its specific gravity is materially decreased. If the temperature is increased, it begins to give off hydrogen at 130°C . It has been suggested that a compound or alloy having the composition Pd_2H is formed; some indications favor this view, but it can hardly be considered as proved at present.

56. Palladium forms two classes of compounds; namely, the palladious compounds, in which this metal is bivalent, and the palladic compounds, in which it is quadrivalent. It is useful, on account of its hardness, lightness, and resistance to tarnish, in the construction of philosophical instruments; alloyed with silver, it is used for small weights. It forms three oxides, Pd_2O , PdO , and PdO_2 , and two chlorides, PdCl_2 and PdCl_4 .

FAMILY 8, SERIES 9

GENERAL REMARKS

57. The elements belonging to Family 8 that fall in Series 9 are *osmium*, *iridium*, and *platinum*. All three are distinguished by their high specific gravity and are comparatively rare, but platinum is the most abundant and useful of them. Just as in Series 3 and 5, the first member, osmium, forms the greatest variety of compounds, and the last member, platinum, shows a tendency to act with a lower valence. This gradation of properties fits Family 8 to act as a connecting link between Families 7 and 1. Thus, manganese forms a great variety of compounds, and tends to act with a high valence; iron resembles manganese but acts with a lower valence; in cobalt the variety of compounds is still further restricted; and nickel acts almost exclusively as a divalent element. Hence, iron, cobalt, and nickel form a connecting link between manganese and copper. In the same way ruthenium, rhodium, and palladium serve to connect molybdenum, and possibly an undiscovered element in Family 7, with silver in Family 1. In a similar manner platinum leads up to gold.

OSMIUM

Symbol *Os*. Atomic weight 190.9. Valence II, III, IV, and VIII.

58. Osmium is always present in the residue from platinum ores, in combination with iridium. In 1804 Tennant showed that the platinum residues contained the two new metals iridium and osmium, the latter so named from the Greek word meaning a *smell*, because of the peculiar odor of the peroxide.

Osmium occurs in the platinum ores as an alloy of iridosmium. Osmium is easily separated from the platinum residues by heating them in a porcelain tube through which a current of air is passed, converting the osmium into the volatile peroxide. This is then mixed with carbon monoxide and passed through a red-hot porcelain tube, when the metal is obtained in the form of a powder. By fusing the powder with tin in a graphite crucible, treating the alloy formed with hydrochloric acid, and heating the residue in a current of hydrochloric-acid gas, the crystalline variety is obtained.

59. Osmium is a bluish-white metal, is harder than glass, and has a specific gravity of 22.48, thus being the heaviest of all bodies. It is almost infusible in the absence of air, but when strongly heated in the air it burns with the formation of the poisonous peroxide. Because of its high melting point, about 2,400° C., osmium is used for the manufacture of incandescent electric lamps, and, alloyed with iridium, for the tips of gold pens.

60. Five oxides of osmium are known: the *monoxide*, OsO , a gray-black powder insoluble in acids; the *sesquioxide*, Os_2O_3 , also black and insoluble in acids; the *trioxide*, OsO_3 ; the *dioxide*, OsO_2 , which forms a copper-colored mass which decomposes in the air; and the extremely poisonous *peroxide*, OsO_4 , which forms colorless prismatic crystals that volatilize below the boiling point of water and have an irritating vapor and odor that affects the eyes and stains the skin black. The oxides OsO , Os_2O_3 , and OsO_2 are bases; OsO_3 forms salts with the bases, forming *osmites*, M_2OsO_4 ; and OsO_4 acts as an indifferent base.

Osmium dichloride, $OsCl_2$, and *osmium tetrachloride*, $OsCl_4$, are obtained as two distinct bodies when the metal is heated in chlorine; $OsCl_2$ is the less volatile, and forms green, needle-like crystals, while $OsCl_4$ is a dark-red powder. By mixing osmium with potassium chloride, heating the mixture in chlorine, treating the mass with water, and evaporating, red octahedral crystals of $K_2OsCl_6 \cdot 3H_2O$ separate.

These effloresce in the air turning pink, and dissolve in water forming a strongly astringent, cherry-red solution.

IRIDIUM

Symbol Ir. Atomic weight 193.1. Valence II, III, and IV.

61. When Tennant discovered osmium and iridium in the residues from platinum ore he found that the salts of the one metal had different colors, and to this metal he gave the name iridium. It is found in platinum ores alloyed with platinum and with osmium. The platinum-iridium alloy is found in the form of small cubes, whereas the osmium-iridium alloy occurs as irregular, flat grains. Iridium is prepared from the latter alloy by fusing with zinc and heating until the zinc is all driven off. The residue is then ignited with barium nitrate, the mass leached with water, and boiled with nitric acid. The iridium is then precipitated as ammonium-iridium chloride and ignited, yielding spongy iridium. This is purified by fusing with lead and treating the resulting mass with nitric acid and with aqua regia.

62. Iridium is a white, steel-like metal with a specific gravity of 22.4. Next to osmium, it is the most difficult metal of the platinum group to fuse, and is the least volatile of this group. It melts at about $2,000^{\circ}\text{C}.$, is very brittle when cold, but somewhat malleable at a white heat. It does not oxidize in the air; it is insoluble in aqua regia unless alloyed with considerable platinum. It unites with chlorine at a low red heat. Alloyed with platinum it forms a hard, elastic compound that takes a fine polish and does not tarnish.

63. *Iridium sesquioxide*, Ir_2O_3 , is the product of the oxidation of finely divided iridium in the air. It is a black powder insoluble in acids, begins to decompose at $800^{\circ}\text{C}.$, and at $1,000^{\circ}\text{C}.$ is converted into the metal and oxygen. The *dioxide*, IrO_2 , is a black powder obtained when the hydroxide is heated in a current of carbon dioxide. The *tetrachloride*, IrCl_4 , is obtained when the finely divided metal is dissolved in aqua regia. The *dichloride*, IrCl_2 , is obtained by heating a solution of the tetrachloride or by passing it over finely divided iridium heated to a red heat. The *trichloride*, IrCl_3 , is prepared by heating a double chloride with sulphuric acid.

PLATINUM

Symbol Pt. Atomic weight 195.2. Valence II and IV.

64. Platinum has been known for many centuries, but was first thoroughly investigated during the 18th century. It was first described by Watson in 1750 and more exactly two years later, in 1752, by Scheffer, who described it as white gold. It derives its name from the Spanish *platina*, meaning little silver. It is found in nature in the metallic state in flattened grains in river sands. It is never pure, being always accompanied by the metals of this group, together with some iron, copper, and gold. The principal source of supply is the Ural Mountains of Russia, though it is also found in Brazil, Peru, Borneo, Australia, and California.

65. **Preparation.**—Platinum is usually prepared by wet methods. The ore is treated with aqua regia until all the platinum is dissolved and is then filtered. The filtrate is treated with lime water until only slightly acid, thus removing the iron, copper, iridium, rhodium, and part of the palladium. The filtrate is evaporated to dryness, ignited, and then washed with dilute hydrochloric acid. The platinum thus obtained is fused with lead, and digested with nitric acid, removing any lead, copper, palladium, and part of the rhodium remaining. The residue is dissolved in aqua regia and the platinum precipitated with ammonium chloride. As the precipitate contains some rhodium, it is fused with potassium bisulphate, leached with water to dissolve the rhodium sulphate formed, the precipitated platinum heated to redness, and then fused into a compact form before the oxyhydrogen blowpipe.

Lately Deville and Debray devised a method that has almost completely superseded the foregoing. In this method the crude platinum is melted with lead and lead sulphide. The alloy of lead and platinum is then melted in a furnace consisting of hollowed out blocks of lime, Fig. 3, in a current of air by means of the oxyhydrogen flame, and is then cast into ingots.

66. Properties.—Pure platinum is a tin-white metal, softer than silver, but is hardened by the presence of other metals, especially iridium. It has a specific gravity of 21.48, melts at $1,775^{\circ}\text{C}$., and can be welded at a white heat. Owing to its low coefficient of expansion, which is very nearly the same as that of glass, it can be sealed into glass without cracking the latter by unequal contraction on cooling. It is not affected by the air, is insoluble in all single acids, but alloys readily with phosphorus, silver, lead, tin, bismuth, arsenic, antimony, etc. It absorbs hydrogen at a red heat and also causes many bodies to combine with oxygen.

Its resistance to the action of acids and to high temperatures renders platinum very valuable in chemical processes. It is

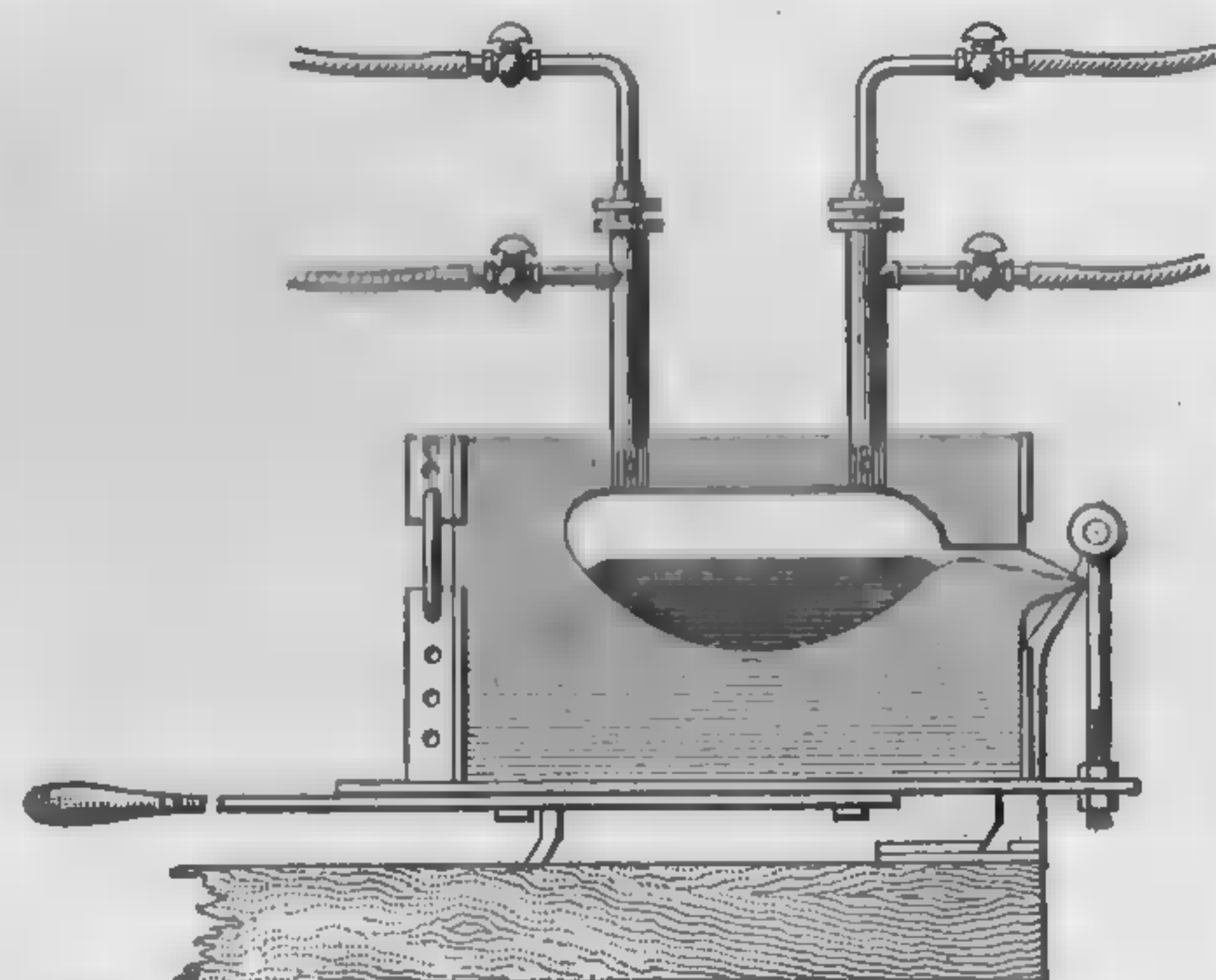


FIG. 3

indispensable to the analytical chemist. It can be easily rolled into thin foil and drawn into fine wires, it having been drawn into a wire $\frac{1}{30000}$ inch in diameter.

67. Platinum, as has already been stated, possesses the power of inducing chemical combination between oxygen

and other gases to a remarkable degree. The spongy as well as the compact metal possesses this property. This can be readily shown by heating a piece of platinum foil to redness in a Bunsen burner, extinguishing the gas, and rapidly turning it on again, when the cold gas will keep the foil at a red heat, in consequence of the combination with atmospheric oxygen at the surface of the platinum. Döbereiner's lamp is founded on this property. Hydrogen passed over spongy platinum in the presence of air is at once ignited owing to its combination with the oxygen of the air condensed within the pores of the metal.

Spongy platinum, in a very active form, is obtained by gently igniting ammonium platonic chloride. This forms a porous

mass of finely divided metallic platinum, which has an extremely large surface compared with its mass.

68. Platinum Black.—When platinum is precipitated in the metallic state from solutions it forms a soft, black powder known as platinum black. It is also obtained when platonic chloride is treated with formaldehyde. This substance has the power of absorbing more than 800 times its volume of oxygen. This oxygen does not combine with the platinum, but is condensed into its pores, and is available for combination with other substances. The power of promoting combination with oxygen is so great that if it is introduced into hydrogen, the oxygen will at once unite with hydrogen and form water. After being heated to redness for a number of times platinum black becomes denser and loses considerable of its activity.

COMPOUNDS OF PLATINUM

69. Oxides of Platinum.—Two oxides of platinum are known. *Platinous oxide*, PtO , prepared by the ignition of the corresponding hydroxide, $\text{Pt}(\text{OH})_2$, is a gray or violet powder that passes into the metal when heated strongly. When heated with a solution of formic acid, a violent evolution of carbon dioxide occurs and platinum black is formed. *Platonic oxide*, PtO_2 , is obtained in a similar manner. *Platonic hydroxide*, $\text{Pt}(\text{OH})_4$, and *platinous hydroxide*, $\text{Pt}(\text{OH})_2$, are obtained by treating the corresponding chlorides with sodium hydroxide. The former is acid in character and forms a few salts of the formula $M_2\text{Pt}(\text{OH})_6$; the latter is an oxidizing agent and acts as a weak base.

70. Chlorides of Platinum.—The most important and best known salt of platinum is *platonic chloride*, PtCl_4 . This may be prepared by heating metallic platinum in chlorine to a temperature of about $1,300^{\circ}\text{C}$. It may also be prepared by dissolving scrap platinum in a mixture of 4 volumes of hydrochloric acid and 1 volume of nitric acid, gently evaporating the solution to a syrupy consistency, redissolving in hydrochloric acid, and again evaporating to a syrup. Care must be taken

not to evaporate too fast or too low, owing to the possibility of forming some metallic platinum. On cooling, the liquid solidifies to a red-brown mass very soluble in water and alcohol, and absorbs moisture from the air. If the solution is allowed to crystallize before all the hydrochloric acid is expelled, brown, prismatic needles of *chloroplatinic acid*, $H_2PtCl_6 \cdot 6H_2O$, are obtained. This compound forms chloroplatinates by the replacement of the hydrogen by metals. With the alkali metals it forms salts that, owing to their great differences in solubility, are very valuable to the analytical chemist.

Potassium chloroplatinate, K_2PtCl_6 , or potassium platonic chloride is precipitated as a yellow crystalline mass when a solution of potassium chloride is added to a solution of chloroplatinic acid. It is slightly soluble in hot water, 5 parts in 100 parts of water, and is insoluble in alcohol.

Sodium chloroplatinate, Na_2PtCl_6 , is obtained in the form of red prisms or tablets and differs from the potassium salt in being readily soluble in water and alcohol.

Rubidium chloroplatinate, Rb_2PtCl_6 , resembles the potassium salt very closely, forms small, yellow, transparent crystals, but is very slightly soluble in water, 100 parts of hot water dissolving only .6 part of the salt. *Cæsium chloroplatinate*, Cs_2PtCl_6 , is the least soluble of the alkali chloroplatinates, only .38 part being dissolved by 100 parts of hot water. *Lithium chloroplatinate*, Li_2PtCl_6 , forms orange-yellow plates, which are efflorescent, and readily soluble in water, but insoluble in ether.

Ammonium chloroplatinate, $(NH_4)_2PtCl_6$, is obtained as a lemon-yellow crystalline mass when chloroplatinic acid is added to an ammonium salt. It is sparingly soluble in water and insoluble in alcohol. When heated, it decomposes without fusion, yielding spongy platinum.

Platinous chloride, $PtCl_2$, is prepared by heating chloroplatinic acid to $300^\circ C.$, when chlorine is evolved. It is also prepared by heating spongy platinum in a current of dry chlorine to $250^\circ C.$ It forms a dingy green powder insoluble in water or in nitric or sulphuric acid. It is soluble in hot hydrochloric acid, yielding a red solution. Heat decomposes it into chlorine and platinum. The hydrochloric-acid solution, when added

to ammonium chloride, yields a double salt, *ammonium chloroplatinite*, $(NH_4)_2PtCl_4$. The *potassium salt*, K_2PtCl_4 , forms rose-colored, crystalline fibers, and forms the starting point for the formation of *chloroplatinous acid*, H_2PtCl_4 , and its salts.

71. Iodides of Platinum.—*Platinic iodide*, PtI_4 , is a dark-brown to black amorphous substance obtained when hydriodic acid acts on a soluble chloroplatinate. It is soluble in hydriodic acid, forming the soluble, unstable compound *iodoplatinic acid*, $H_2PtI_6 \cdot 9H_2O$. *Platinous iodide*, PtI_2 , is formed as a black powder when platinous chloride and potassium iodide are boiled together.

A SERIES OF QUESTIONS AND EXAMPLES

RELATING TO THE SUBJECTS
TREATED OF IN THIS VOLUME

It will be noticed that the various Examination Questions that follow have been given the same section numbers as the Instruction Papers to which they refer. No attempt should be made to answer any of the questions or to solve any of the examples until the Instruction Paper having the same section number has been carefully studied.

INORGANIC CHEMISTRY

(PART 1)

EXAMINATION QUESTIONS

Notice to Students.—*Study the Instruction Paper thoroughly before you attempt to answer these questions. Read each question carefully and be sure you understand it; then write the best answer you can. When your answers are completed, examine them closely and correct all the errors you can find; then mail them to us.*

- (1) Define matter.
- (2) State the law regarding the effect of heat on the volume of gases.
- (3) (a) Define a physical change. (b) Give an example of a physical change.
- (4) What is the weight, expressed in the metric system, of 1 cubic centimeter of pure distilled water at 4° C.?
- (5) Name the elements that are at ordinary temperatures: (a) liquids; (b) gases.
- (6) Define: (a) a molecule; (b) an atom.
- (7) (a) Name three forms of matter. (b) Give one example of each form.
- (8) State the law regarding the indestructibility of matter.
- (9) Define atomic weight.
- (10) How many cubic centimeters are contained in 1 liter?
- (11) State how metals and non-metals differ: (a) chemically; (b) physically.

(12) State the valence of each element in the following compounds: (a) $Cl-Ca-Cl$; (b) $H-O-H$; (c) $K-O-K$; (d) $O=Fe-O-Fe=O$; (e) $O=\overset{\overset{O}{\parallel}}{S}=O$. (*Cl* is chlorine, *Ca* is

calcium, *H* is hydrogen, *O* is oxygen, *Fe* is iron, and *S* is sulphur.)

(13) State the law governing the effect of pressure on the volume of gases.

(14) Define density.

(15) State the law of Avogadro.

(16) Define: (a) effervescence; (b) efflorescence; (c) deliquescence.

(17) What is the weight of 1 liter of pure distilled water at 4° C.?

(18) (a) Define energy. (b) Name three forms of energy.

(19) (a) Define chemical change. (b) Give an example of a chemical change.

(20) The formula of water is H_2O . State how many atoms it contains of: (a) oxygen; (b) hydrogen. The formula of two molecules of water is $2H_2O$. State how many atoms it contains of: (c) oxygen; (d) hydrogen.

INORGANIC CHEMISTRY

(PART 2)

EXAMINATION QUESTIONS

- (1) Name three materials in which hydrogen occurs.
- (2) Write the chemical equation that graphically represents the change taking place when zinc is acted on by sulphuric acid in the preparation of hydrogen.
- (3) What is produced when electric sparks are passed through air or oxygen?
- (4) Describe the preparation of Schönbein's test paper.
- (5) Where does oxygen occur?
- (6) Give some of the properties of oxygen.
- (7) Write the chemical equation that graphically represents the change taking place when sodium acts on water.
- (8) State what is meant by collection of a gas: (a) by downward displacement; (b) by upward displacement.
- (9) Name three uses for the oxyhydrogen blowpipe.
- (10) What is the composition of water by volume?
- (11) Give some of the properties of hydrogen peroxide.
- (12) Write the chemical equation showing the change that takes place when lime is slaked.
- (13) Give some of the properties of ozone.
- (14) Where does water occur?

(15) Write the chemical equation that graphically represents the decomposition of potassium chlorate when preparing oxygen.

(16) Give some of the properties of water.

(17) Give several of the principal properties of hydrogen.

(18) What is the composition of water by weight?

(19) Name two uses of ozone.

(20) Write the chemical equation representing the formation of: (a) phosphorus pentoxide from phosphorus and oxygen; (b) carbon dioxide from carbon and oxygen; (c) sodium oxide from sodium and oxygen; (d) sulphur dioxide from sulphur and oxygen.

INORGANIC CHEMISTRY

(PART 3)

EXAMINATION QUESTIONS.

(1) Define: (a) combustion; (b) kindling temperature; (c) explosion.

(2) (a) Name the three classes into which salts are divided. (b) Illustrate each class by means of a formula.

(3) Define: (a) acids; (b) bases; (c) salts.

(4) Name each of the following acids: (a) HCl ; (b) $HClO$; (c) $HClO_2$; (d) $HClO_3$; (e) $HClO_4$.

(5) (a) Define a reducing agent. (b) Illustrate, by means of an equation, a reducing reaction. (c) Name five reducing agents.

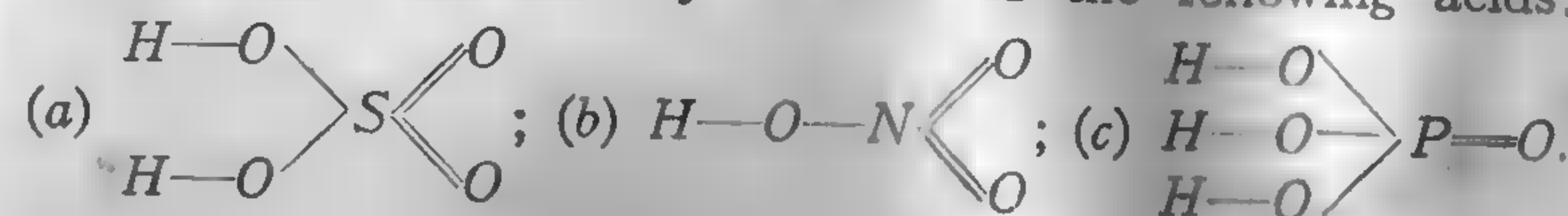
(6) (a) Define an oxidizing agent. (b) Illustrate, by means of an equation, an oxidizing reaction. (c) Name five oxidizing agents.

(7) One liter of hydrogen unites with one liter of chlorine to form how many liters of hydrochloric acid? (See Art. 21.)

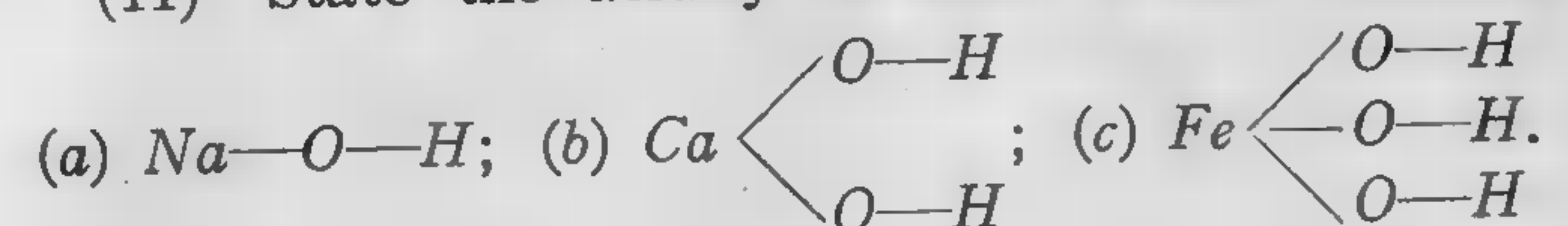
(8) State the two laws established by Berthollet.

(9) Define: (a) neutralization; (b) allotropy.

(10) State the basicity of each of the following acids:



(11) State the acidity of each of the following bases:



(12) Name each of the following salts: (a) KCl ; (b) KClO ; (c) KClO_2 ; (d) KClO_3 ; (e) KClO_4 .

(13) A gas occupies 250 liters at a pressure of 745 mm. and a temperature of -15°C . What volume will it occupy if the pressure is raised to 765 mm. and the temperature to 20°C .?

(14) The formula of magnesium pyrophosphate is $\text{Mg}_2\text{P}_2\text{O}_7$. What is the percentage quantity of each element in the compound?

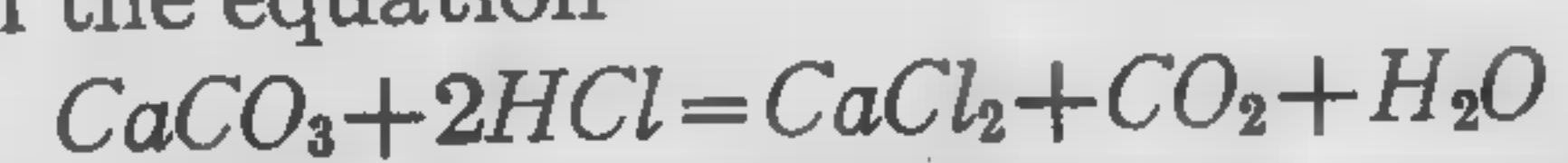
(15) State the periodic law.

(16) Define: (a) precipitation; (b) precipitate; (c) precipitant.

(17) Name each of the following substances: (a) FeO ; (b) Fe_2O_3 ; (c) SnCl_2 ; (d) SnCl_4 .

(18) (a) Name the two kinds of thermochemical reactions. (b) Define each of them.

(19) From the equation



calculate the number of grams of calcium carbonate dissolved by 100 grams of hydrochloric acid.

(20) Calculate the percentage of: (a) lead in PbSO_4 ; (b) antimony in Sb_2O_4 .

INORGANIC CHEMISTRY

(PART 4)

EXAMINATION QUESTIONS

(1) Complete the equation $2\text{NaBr} + \text{Cl}_2 = ?$

(2) What are the properties of chloric acid?

(3) Chlorine, bromine, and iodine are said to be members of one family of elements; give a comparison of their properties and name some of their compounds to show why they are so described.

(4) (a) How does chlorine occur in nature? (b) Describe two processes for the preparation of chlorine, and give an equation in each case.

(5) (a) How does bromine occur in nature? (b) Describe its preparation and give its properties.

(6) (a) What is the usual rule for preparing an acid? (b) What are the two prominent exceptions to this rule?

(7) Give a description of the method of preparing perchloric acid.

(8) How would you show the relative stability of the compounds of chlorine, bromine, and iodine?

(9) Give the formula of bleaching powder and tell how it is prepared.

(10) Describe the preparation of hydriodic acid.

(11) What elements constitute the halogen group?

(12) Give the method of preparation and the properties of chlorine monoxide.

(13) (a) Complete the following equation: $2NaI + MnO_2 + 2H_2SO_4 = ?$ (b) Express this equation in words.

(14) How does chlorine act as a bleaching agent?

(15) (a) Describe the preparation of hydrofluoric acid. (b) Describe fully the action of hydrofluoric acid on glass.

(16) Give the preparation and properties of fluorine.

(17) What are the properties of hydrochloric acid?

(18) How many oxides and acids does chlorine form, and what are they?

(19) (a) What oxides and acids do bromine and iodine form? (b) Name them.

(20) Describe the method of preparing iodine from kelp.

INORGANIC CHEMISTRY

(PART 5)

EXAMINATION QUESTIONS

(1) Give the principal reactions that occur in the lead chambers in the manufacture of sulphuric acid.

(2) By what tests could you prove that a substance that is said to be sulphur, actually is that element?

(3) What elements belong to Family 6, Group B?

(4) (a) How is sulphur dioxide prepared? (b) Give its properties.

(5) (a) How is sulphur commonly obtained? (b) Give its properties.

(6) State the formula of selenic acid.

(7) Mention the compounds of sulphur that occur in nature.

(8) What weight of sulphur is contained in 100 grams of hydrogen sulphide?

(9) Describe the behavior of sulphur under the influence of varying amounts of heat.

(10) What is the result, in each instance, when hydrogen sulphide is passed into test tubes containing solutions of sodium arsenite, copper sulphate, and antimony chloride?

(11) Calculate the weight of 100 liters of hydrogen sulphide at 0° and 760 mm.

- (12) State the properties of tellurium.
- (13) How is hyposulphurous acid, H_2SO_2 , prepared?
- (14) Give the properties of sulphur trioxide and write its formula.
- (15) Describe the preparation of hydrogen sulphide.
- (16) How is sulphuric acid detected?
- (17) What is disulphuric acid, and how is it made?
- (18) Ten grams of S gives how many grams of SO_2 ?
- (19) How may sulphur be detected both in the free state and when combined?
- (20) What oxides and acids does sulphur form?

INORGANIC CHEMISTRY

(PART 6)

EXAMINATION QUESTIONS

- (1) Name the constituents of the atmosphere.
- (2) Calculate the percentage composition of phosphine.
- (3) How may nitrogen be prepared?
- (4) Give the formula for Scheele's green.
- (5) Give the chemical changes in making phosphorus.
- (6) Two hundred and fifty cubic centimeters of nitrogen, at normal temperature and pressure, weighs how much?
- (7) State some reasons for believing that air is a mechanical mixture and not a compound of oxygen and nitrogen.
- (8) Give the names of the following compounds:
 H_2NaPO_4 , $HCaPO_4$, $BiPO_4$.
- (9) Give the properties of antimony.
- (10) One hundred liters of nitric oxide at $0^\circ C$. and 760 millimeters is required to complete an operation at a chemical plant. What weight of copper is necessary to produce it?
- (11) (a) Describe Marsh's test. (b) What is the limit of its delicacy?
- (12) Give the properties of arsenic trioxide.
- (13) Name and give formulas of the oxides of (a) bismuth; (b) antimony.

(14) How many grams of slaked lime are necessary to prepare 68 grams of ammonia?

(15) What general methods would you use to prepare a nitrate from nitric acid?

(16) Compare the properties of common phosphorus with those of allotropic phosphorus.

(17) What is the best antidote in case of arsenic poisoning?

(18) What weight of phosphorus pentoxide can be obtained by burning 793 grams of phosphorus in oxygen?

(19) How is arsenic separated from its ores?

(20) State how you would prove the presence of copper arsenite in a bright-green colored piece of wall paper.

INORGANIC CHEMISTRY

(PART 7)

EXAMINATION QUESTIONS

(1) Required 264 grams of carbon dioxide. (a) How can it be prepared? (b) What weight of calcium carbonate will be required to produce it?

(2) (a) Define destructive distillation. (b) Give an example of it.

(3) For what is thorium dioxide largely used?

(4) Describe in detail the commercial manufacture of illuminating gas.

(5) (a) How can artificial diamonds be made? (b) Are they of commercial value?

(6) (a) Name the different classes of coal. (b) Give the fixed carbon content of each class.

(7) What advantage has the by-product coke oven over the beehive oven?

(8) Outline the process of manufacturing coke in the by-product oven.

(9) How is acetylene gas commercially prepared?

(10) Write two equations showing the preparation of carbon dioxide.

(11) Define: (a) normal carbonate; (b) acid carbonate; (c) basic carbonate.

(12) Write the equation showing the change that takes place when carbon monoxide is passed over red-hot copper oxide.

(13) How many liters of carbon dioxide are formed when 2 liters of carbon monoxide unite with 1 liter of oxygen? (See page 30.)

(14) Draw a sketch of a Bunsen burner and tell how it is used.

(15) Define: (a) a combustible; (b) a supporter of combustion.

(16) On what principle is the construction of the miner's safety lamp based?

(17) What weight of carbon dioxide is formed by burning 48 grams of carbon? Ans. 176 grams

(18) (a) State how water gas is prepared; (b) of what gases does it generally consist?

(19) What salts in water produce (a) temporary hardness; (b) permanent hardness?

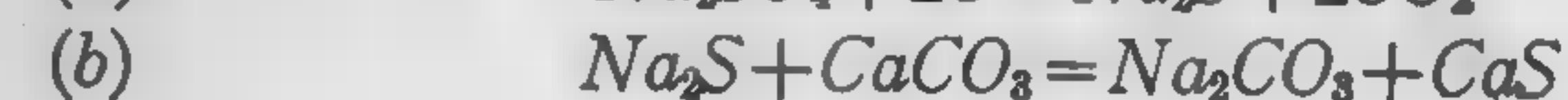
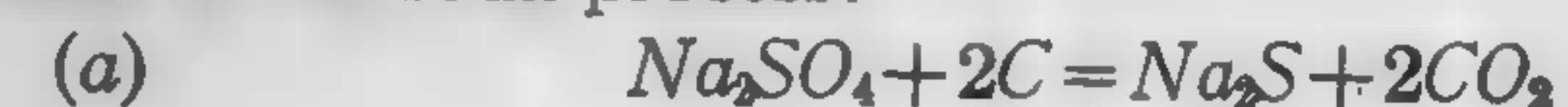
(20) Give two ways of preparing methane.

INORGANIC CHEMISTRY

(PART 8)

EXAMINATION QUESTIONS

(1) How much sodium carbonate will 75 kilograms of sodium sulphate yield if the following equations are made the basis of the soda process?



(2) Describe the preparation of potassium and give its general properties.

(3) Give the formula of ammonium bicarbonate, and state how it may be prepared.

(4) Show, by means of an equation, the products obtained by the action of chlorine on a concentrated solution of potassium hydroxide.

(5) Give symbol, atomic weight, and properties of lithium.

(6) Give the preparation and properties of sodium.

(7) What weight of potassium hydroxide will 70 kilograms of potassium carbonate yield?

(8) Give the formula of ammonium nitrate, and mention one of its uses.

(9) What is the percentage composition of common salt?

(10) State the properties and give the formula of potassium sulphate.

(11) Give the formula and principal properties of potassium hydroxide.

(12) How does gold occur in nature?

(13) Mention the properties of metallic copper.

(14) Give the principal properties of silver chloride, and mention the name of the mineral in which it occurs in nature.

(15) What percentage of silver does silver nitrate contain?

(16) What weight of copper can be obtained from 1,000 kilograms of pure malachite?

(17) State the principal properties and give the formula of copper sulphate.

(18) Give the formulas of the chlorides of gold, and state how they may be prepared.

(19) What weight of silver is required to prepare 250 grams of silver nitrate?

(20) Describe the preparation and the principal properties of silver bromide.

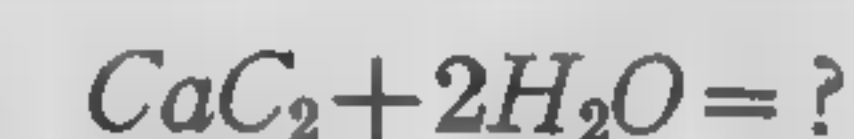
INORGANIC CHEMISTRY

(PART 9)

EXAMINATION QUESTIONS

(1) What is so-called galvanized iron?

(2) Complete the following equation and name the factors and products:



(3) Give the symbol, atomic weight, and valence of: (a) indium; (b) scandium.

(4) How does barium occur in nature?

(5) How much lime can be obtained from 150 kilograms of calcium carbonate?

(6) State what you know about the occurrence of zinc.

(7) How much calcium hydroxide can be obtained from 250 kilograms of lime?

(8) (a) Under what names does aluminum oxide occur in nature? (b) Describe a method for the preparation of metallic aluminum.

(9) State how barium oxide is obtained and give its properties.

(10) What is the chief use of anhydrous calcium chloride in the laboratory?

(11) Give the formula of borax and state where it is found.

- (12) How is plaster of Paris obtained?
- (13) State what you know about cadmium sulphide.
- (14) Give the formula: (a) of mercurous sulphate; (b) of mercuric sulphate.
- (15) Name the compounds having the formulas: (a) $Tl(OH)_3$; (b) $TlCl$.
- (16) How is glucinum chloride prepared?
- (17) Give the properties of magnesium.
- (18) Name and give the composition of the minerals in which strontium occurs in nature.
- (19) In what minerals does yttrium occur?
- (20) Describe the Belgian process for the manufacture of zinc.

INORGANIC CHEMISTRY

(PART 10)

EXAMINATION QUESTIONS

- (1) Give the formulas of: (a) the oxides of columbium; (b) the oxides of manganese.
- (2) Give the formula of germanium tetrachloride.
- (3) Give the formula of: (a) potassium chromate; (b) lead chromate.
- (4) Describe the preparation of uranium, and give its properties.
- (5) How is white lead prepared?
- (6) In what form does tin occur in nature?
- (7) What are the objections to the use of lead water pipes?
- (8) (a) How does chromium occur in nature? (b) How is the name derived?
- (9) What percentage of manganese does manganic oxide contain?
- (10) How does: (a) molybdenum occur in nature? (b) tungsten? (c) manganese?
- (11) Give the formulas of the oxides of tantalum.
- (12) What weight of tin is necessary for the preparation of 950 grams of stannic chloride?
- (13) Give the formula of molybdenite.

(14) Give the formula of molybdenum pentachloride, and state how it is prepared.

(15) Give the formula of tungsten trioxide, and state how it is prepared.

(16) Mention the principal minerals in which lead occurs.

(17) Write the chemical reactions that occur in obtaining lead from galena.

(18) What valence has chromium in its oxides?

(19) Give the formula of chrome yellow, and state for what it is used.

(20) Give the formulas of the oxides of vanadium.

INORGANIC CHEMISTRY

(PART 11)

EXAMINATION QUESTIONS

(1) Mention some of the most important physical properties of iron.

(2) What percentage of nickel does pure niccolite contain?

(3) What weight of cobaltous oxide is required to yield 36 grams of anhydrous cobaltous nitrate?

(4) (a) What is the composition of hematite? (b) What percentage of iron does it theoretically contain?

(5) Mention the properties of palladium.

(6) Describe the preparation of nickel.

(7) (a) How is ferrous sulphate prepared? (b) How is anhydrous ferric chloride obtained?

(8) Mention the properties of cobalt.

(9) Describe the different methods of obtaining pure platinum.

(10) With what other elements is platinum usually associated in nature?

(11) Describe the principles of Döbereiner's lamp.

(12) Give the formula and properties of nickel carbonyl.

(13) What remarkable property distinguishes platinum black?

- (14) Give the formulas of the three oxides formed by rhodium.
- (15) What element absorbs, or occludes, hydrogen?
- (16) How is ruthenium peroxide prepared?
- (17) Give the formulas of the oxides of osmium.
- (18) What is the heaviest substance known?
- (19) Give the properties of nickel, and state its principal uses.
- (20) (a) Describe the preparation of iridium. (b) Give the name and formulas of the chlorides of iridium, and state how they are prepared.

A KEY

TO ALL THE QUESTIONS AND EXAMPLES
INCLUDED IN THE EXAMINATION QUESTIONS.

It will be noticed that the Keys have been given the same section numbers as occur on the headlines of Examination Questions to which they refer. All article references refer to the Instruction Paper bearing the same section number as the Key in which it occurs, unless the title of some other Instruction Paper is given in connection with the article number.

To be of the greatest benefit, the Keys should be used sparingly. They should be used much in the same manner as a pupil would go to a teacher for instruction with regard to answering some example he was unable to solve. If used in this manner, the Keys will be of great help and assistance to the student, and will be a source of encouragement to him in studying the various papers composing the Course.

INORGANIC CHEMISTRY

(PART 1)

- (1) See Art. 2.
- (2) See Art. 24.
- (3) (a) and (b) See Art. 4.
- (4) See Art. 32.
- (5) (a) and (b) See Art. 16.
- (6) (a) and (b) See Art. 5.
- (7) (a) and (b) See Art. 9.
- (8) See Art. 11.
- (9) See Art. 16.
- (10) See Art. 32.
- (11) (a) and (b) See Art. 31.
- (12) The valence of: (a) *Cl* is 1, *Ca* is 2; (b) *H* is 1, *O* is 2. (c) *K* is 1, *O* is 2; (d) *Fe* is 3, *O* is 2; (e) *S* is 6, *O* is 2.
- (13) See Art. 25.
- (14) See Art. 27.
- (15) See Art. 26.
- (16) (a), (b), and (c) See Art. 48.
- (17) See Art. 32.
- (18) (a) and (b) See Art. 3.
- (19) (a) and (b) See Art. 4.
- (20) (a) 1 atom of oxygen; (b) 2 atoms of hydrogen; (c) 2 atoms of oxygen; (d) 4 atoms of hydrogen.

INORGANIC CHEMISTRY

(PART 2)

- (1) See Art. 2.
- (2) $Zn + \begin{array}{c} H-O \\ H-O \end{array} \rangle S \begin{array}{c} O \\ O \end{array} = Zn \begin{array}{c} O \\ O \end{array} \rangle S \begin{array}{c} O \\ O \end{array} + H-H.$ See Art. 4.
- (3) See Art. 17.
- (4) See Art. 19.
- (5) See Art. 10.
- (6) See Art. 14.
- (7) $2H-O-H + Na + Na = 2Na-O-H + H-H.$ See Art. 3.
- (8) (a) and (b). See Art. 25.
- (9) See Art. 39.
- (10) Water contains 2 volumes of hydrogen to 1 volume of oxygen.
See Art. 37.
- (11) See Art. 42.
- (12) $CaO + H_2O = Ca(OH)_2.$ See Art. 33.
- (13) See Art. 18.
- (14) See Art. 27.
- (15) $2K-O-Cl \begin{array}{c} O \\ O \end{array} = 2K-Cl + 3O = O.$ See Art. 11.
- (16) See Art. 29.
- (17) See Arts. 5 and 6.
- (18) Water contains 7.94 parts by weight of oxygen to 1 part by weight of hydrogen. See Art. 38.
- (19) See Art. 21.
- (20) See Art. 14.

INORGANIC CHEMISTRY

(PART 3)

- (1) (a) See Art. 1.
(b) See Art. 2.
(c) See Art. 3.
- (2) (a) and (b) See Art. 15.
- (3) (a) See Art. 6.
(b) See Art. 7.
(c) See Art. 9.
- (4) See Table II, page 19.
- (5) (a), (b), and (c) See Art. 5.
- (6) (a), (b), and (c) See Art. 4.
- (7) See Art. 21, page 24.
- (8) See Arts. 11 and 12.
- (9) (a) See Art. 8.
(b) See Art. 10.
- (10) See Art. 13. (a) dibasic; (b) monobasic; (c) tribasic.
- (11) See Art. 14. (a) monacid; (b) diacid; (c) triacid.
- (12) (a) Potassium chloride; (b) potassium hypochlorite; (c) potassium chlorite; (d) potassium chlorate; (e) potassium perchlorate.
- (13) See Art. 32, Case III. Substituting the correct values in the formula $V' = \frac{T' P V}{T P'}$,

$$V' = \frac{(273+20) \times 745 \times 250}{(273-15) \times 765} = 276.49 \text{ liters. Ans.}$$
- (14) The molecular weight of $Mg_2P_2O_7$ is $(24 \times 2) + (31 \times 2) + (16 \times 7)$, or $48 + 62 + 112 = 222$.

INORGANIC CHEMISTRY

(PART 5)

- (1) See Arts. 32 and 33.
- (2) See Art. 6.
- (3) See Art. 1.
- (4) (a) and (b) See Art. 23.
- (5) (a) See Art. 3.
(b) See Art. 4.
- (6) H_2SeO_4 . See also Art. 48.
- (7) See Art. 2.
- (8) The molecular weight of hydrogen sulphide is 34.086 and the atomic weight of sulphur is 32.07; hence, by proportion, we have:
 $34.086 : 32.07 = 100 : x$. $x = 94.086$. Ans.
- (9) See Art. 4.
- (10) See Art. 15.
- (11) The density of hydrogen sulphide is 17; hence, 1 liter weighs $17 \times .089873 = 1.52784$ grams, and 100 liters weighs $1.52784 \times 100 = 152.784$ grams. Ans.
- (12) See Art. 54.
- (13) See Art. 21.
- (14) See Art. 29. Its formula is SO_3 .
- (15) See Arts. 11 and 12.
- (16) See Art. 39.
- (17) See Art. 38.
- (18) The atomic weight of sulphur is 32.07, and the molecular weight of SO_2 is 64.07. Hence, by proportion, we have:
 $32.07 : 64.07 = 10 : x$. $x = 19.978$ grams. Ans.
- (19) See Art. 6.
- (20) See Art. 20.

INORGANIC CHEMISTRY

(PART 6)

(1) See Art. 9.

(2) Phosphine is PH_3 . $P=31$, $3H=3$; hence, $PH_3=34$.
 $31 \times 100 \div 34 = 91.18$ per cent. phosphorus
 $3 \times 100 \div 34 = 8.82$ per cent. hydrogen

(3) See Arts. 3 and 4.

(4) $CuHASO_8$. See Art. 73.

(5) See Art. 46.

(6) As the density of nitrogen is 14 and 1 liter of hydrogen at normal temperature and pressure weighs .089873 gram, 1 liter of nitrogen at the same temperature and pressure weighs $.089873 \times 14 = 1.258$ grams, 1 liter contains 1,000 cubic centimeters; therefore, 250 cubic centimeters $= \frac{1}{4}$ liter. Hence, $1.258 \div 4 = .3145$ gram. Ans.

(7) See Art. 12.

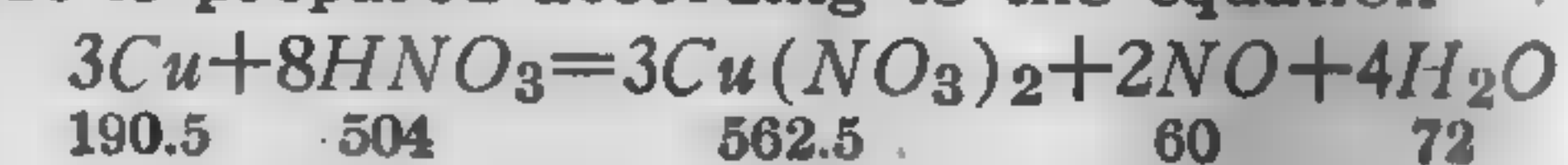
(8) H_2NaPO_4 , primary sodium phosphate; $HCaPO_4$, acid calcium phosphate; $BiPO_4$, bismuth phosphate.

(9) See Art. 85.

(10) As the density of nitric oxide is 15 and the weight of 1 liter of hydrogen at 0° C. and 760 mm. pressure is .089873 gram, 100 liters of nitric oxide at the same temperature and pressure will weigh

$$.089873 \times 15 \times 100 = 134.8095 \text{ grams}$$

Nitric oxide is prepared according to the equation



Hence, by proportion, we have

$$60 : 190.5 = 134.8095 : x. \quad x = 428.02 \text{ grams. Ans.}$$

(11) (a) and (b) See Art. 69.

(12) See Art. 72.

(13) (a) See Art. 98.

(b) See Art. 87.

- (14) Ammonia is prepared according to the equation,

$$\underset{107}{2\text{NH}_4\text{Cl}} + \underset{74}{\text{Ca}(\text{OH})_2} = \underset{111}{\text{CaCl}_2} + \underset{36}{2\text{H}_2\text{O}} + \underset{34}{2\text{NH}_3}$$

Hence, by proportion, we have

$$34 : 74 = 68 : x. \quad x = 148 \text{ grams. Ans.}$$

- (15) A nitrate may be prepared by adding nitric acid to a metal, a base, or a carbonate. See Art. 42.

- (16) See Arts. 47 and 48.

- (17) The best antidote in case of arsenic poisoning is freshly precipitated ferric hydroxide. See Art. 72.

- (18)
$$\underset{124}{\text{P}_4} + \underset{160}{5\text{O}_2} = \underset{284}{2\text{P}_2\text{O}_5}$$

$$124 : 284 = 793 : x. \quad x = 1816.22 \text{ grams } \text{P}_2\text{O}_5. \text{ Ans.}$$

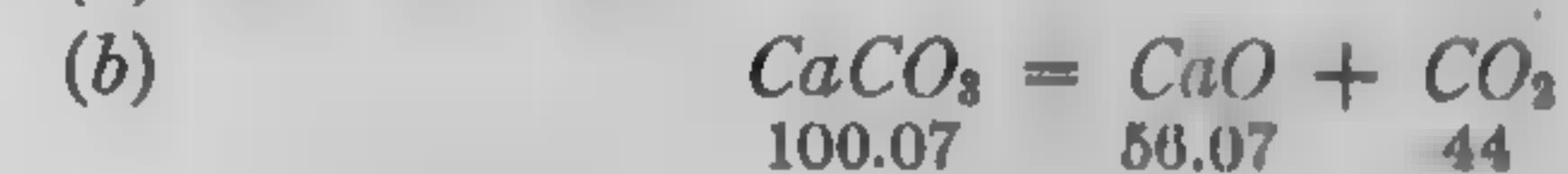
- (19) See Art. 68.

- (20) See Art. 73.

INORGANIC CHEMISTRY

(PART 7)

- (1) (a) See Art. 20.



Hence, by proportion:

$$44 : 100.07 :: 264 : x; \quad x = 600.42 \text{ grams } \text{CaCO}_3$$

- (2) (a) and (b) See Art. 3.

- (3) See Art. 82.

- (4) See Art. 15.

- (5) See Art. 4; (a) page 3; (b) page 4.

- (6) (a) and (b) See Art. 4, page 5.

- (7) See Art. 4, page 7.

- (8) See Art. 4, pages 7 and 8.

- (9) See Art. 14.

- (10) See Art. 20.

- (11) (a), (b), and (c) See Art. 26.

- (12) See Art. 33.
$$\text{CuO} + \text{CO} = \text{Cu} + \text{CO}_2$$

- (13) See Art. 36.
$$\underset{2 \text{ vol.}}{2\text{CO}} + \underset{1 \text{ vol.}}{\text{O}_2} = \underset{2 \text{ vol.}}{2\text{CO}_2}$$

Hence, 2 liters of CO unite with 1 liter of O₂ to form 2 liters of CO₂.

- (14) See Art. 43, page 36.

- (15) See Art. 37.

- (16) See Art. 44.

- (17)
$$\underset{12}{\text{C}} + \underset{32}{\text{O}_2} = \underset{44}{\text{CO}_2}$$

Hence, by proportion:

$$12 : 44 :: 48 : x; \quad x = 176 \text{ grams } \text{CO}_2$$

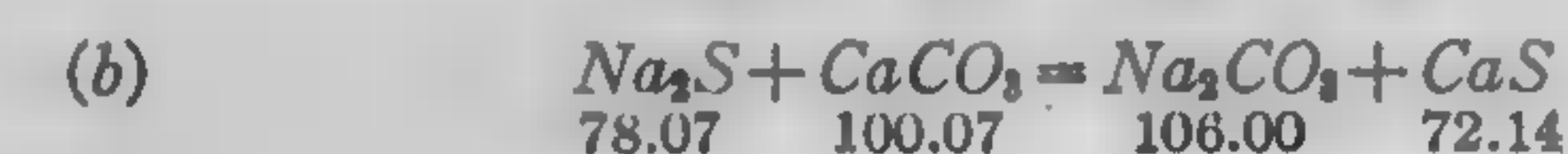
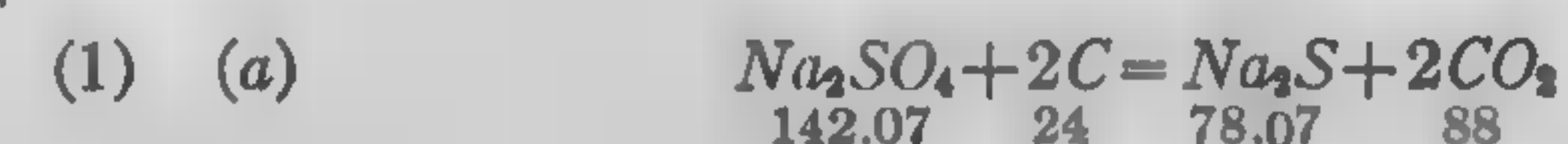
- (18) See Art. 34.

- (19) See Art. 27.

- (20) See Art. 9.

INORGANIC CHEMISTRY

(PART 8)



As 1 molecule of Na_2SO_4 yields 1 molecule of Na_2CO_3 , and as their atomic weights are 142.07 and 106, respectively, we have the proportion:

$$142.07 : 106 = 75 : X. \quad X = 55.95 + \text{Kg. Na}_2\text{CO}_3. \quad \text{Ans.}$$

(2) See Art. 4.

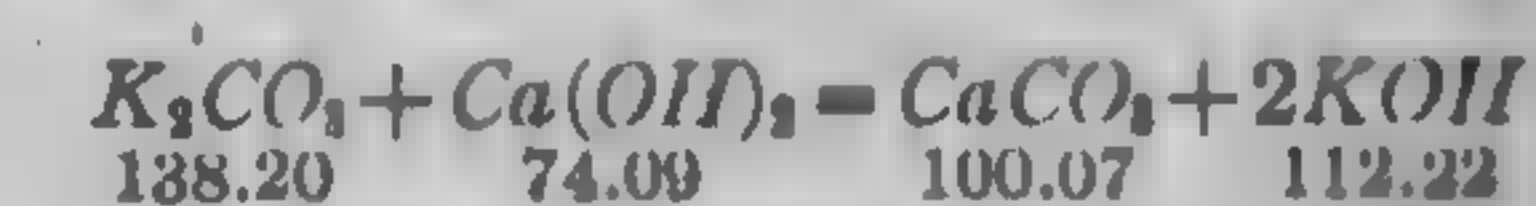
(3) See Art. 45.

(4) See Art. 13.

(5) Symbol *Li*. Atomic weight 6.94. For its properties see Art. 53.

(6) See Art. 24.

(7) Potassium hydroxide is prepared from the carbonate according to the equation:



As 138.20 parts of K_2CO_3 yields 112.22 parts of KOH , we have, by proportion:

$$138.2 : 112.22 = 70 : X. \quad X = 56.84 + \text{Kg. KOH.} \quad \text{Ans.}$$

(8) See Art. 42.

(9) The molecular weight of sodium chloride is 58.46, composed of 23 parts of sodium and 35.46 parts of chlorine. Dividing the parts by the whole to get the percentage, we have:

$$23 \div 58.46 = 39.34\% \text{ Na}$$

$$35.46 \div 58.46 = 60.66\% \text{ Cl}$$

(10) See Art. 11.

(11) See Art. 5.

(12) See Art. 89.

(13) See Art. 64.

(14) See Art. 81.

(15) As the molecular weight of silver nitrate is 169.89, and the weight of silver in it is 107.88, we have:

$$107.88 \div 169.89 = 64.08\% \text{ Ag. Ans.}$$

(16) The formula of pure malachite is $\text{Cu}_2(\text{OH})_2\text{CO}_3$; its molecular weight is 221.16, and the weight of copper in a molecule is 127.14. Hence, by proportion, we have:

$$221.16 : 127.14 = 1,000 : X. \quad X = 574.82 + \text{Kg. Cu. Ans.}$$

(17) See Art. 72.

(18) See Art. 93.

(19) For the preparation of 1 molecule of AgNO_3 weighing 169.89, 1 atom of Ag, weighing 107.88, is required. Hence,

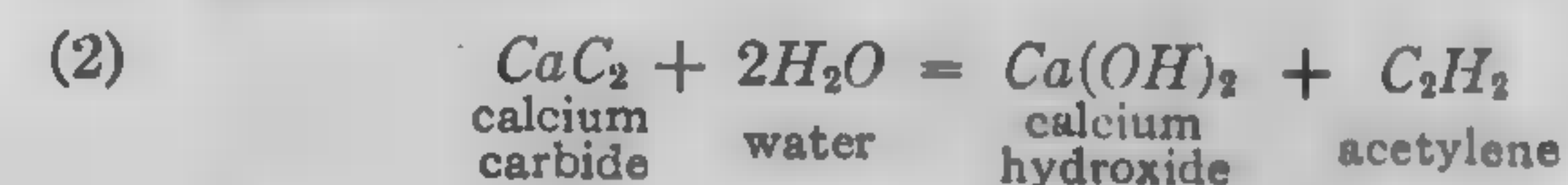
$$169.89 : 107.88 = 250 : X. \quad X = 158.74 + \text{grams Ag. Ans.}$$

(20) See Art. 82.

INORGANIC CHEMISTRY

(PART 9)

(1) See Art. 53.

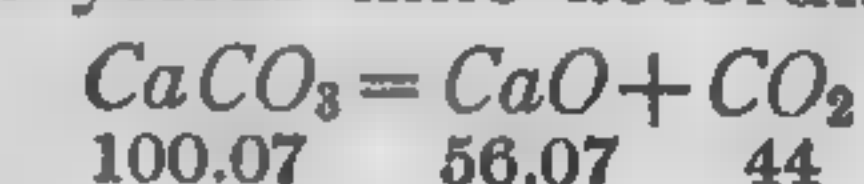


(3) (a) Symbol *In*; atomic weight, 114.8; valence II and III.

(b) See Art. 98.

(4) See Art. 26.

(5) Calcium carbonate yields lime according to the equation:

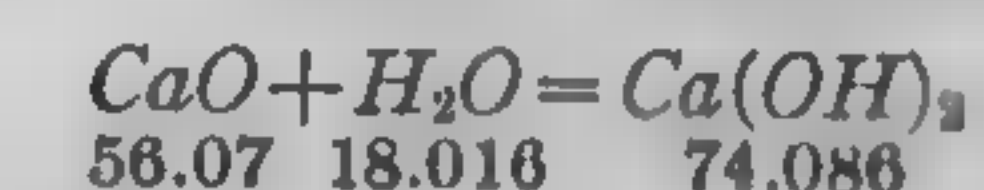


Hence, by proportion, we have:

$$100.07 : 56.07 = 150 : x. \quad x = 84.04 \text{ kg. lime. Ans.}$$

(6) See Art. 51.

(7) Calcium hydroxide is obtained from lime according to the equation:



Hence, by proportion, we have:

$$56.07 : 74.086 = 250 : x. \quad x = 330.32 + \text{kg. Ca}(\text{OH})_2. \text{ Ans.}$$

(8) (a) See Art. 91.

(b) See Art. 89.

(9) See Art. 28.

(10) See Art. 6.

(11) See Art. 87.

(12) See Art. 10.

(13) See Arts. 62 and 66.

(14) (a) and (b) See Art. 78.

(15) (a) and (b) See Art. 112.

(16) See Art. 40.

(17) See Art. 43.

(18) See Art. 18.

(19) See Art. 99.

(20) See Art. 52.

INORGANIC CHEMISTRY

(PART 10)

- (1) (a) See Art. 41.
(b) Manganese dioxide, MnO_2 ; manganous oxide, MnO ; manganic oxide, Mn_2O_3 ; red oxide of manganese, Mn_2O_4 ; manganese heptoxide, Mn_2O_7 .
- (2) $GeCl_4$.
- (3) (a) See Art. 59.
(b) See Art. 63.
- (4) See Arts. 74 and 75.
- (5) See Art. 34.
- (6) See Art. 3.
- (7) See Art. 21.
- (8) (a) and (b) See Art. 48.
- (9) As the atomic weight of manganese is 54.93, $Mn_2=109.86$; and as the atomic weight of oxygen is 16.0, $O_3=48.0$; hence, the molecular weight of $Mn_2O_3=157.86$. Dividing the weight of manganese in the molecule by the molecular weight, we have:
- $$109.86 \div 157.86 = 69.59\% \text{ Mn. Ans.}$$
- (10) (a) See Art. 65.
(b) See Art. 70.
(c) See Art. 82.
- (11) See Art. 43.
- (12) As the atomic weight of tin is 119.0 and of chlorine 35.46, the molecular weight of stannic chloride is 260.84. Hence, by proportion, we have:
- $$260.84 : 119.0 = 950 : x. \quad x = 433.407. \text{ Ans.}$$
- (13) See Art. 67.

(14) See Art. 68.

(15) See Art. 71.

(16) See Art. 14.

(17) See Arts. 15, 16, and 17.

(18) In Cr_2O_3 chromium appears to be trivalent, and in CrO_3 it appears to be hexavalent.

(19) See Art. 35.

(20) See Art. 39.

INORGANIC CHEMISTRY

(PART 11)

(1) See Art. 3.

(2) The formula of niccolite is $NiAs$, its molecular weight is 133.64, and the atomic weight of nickel is 58.68. Hence,

$$58.68 + 133.64 = 43.91\% \text{ Ni. Ans.}$$

(3) The molecular weight of cobaltous oxide is 74.97 and of cobaltous nitrate is 182.99. Hence, by proportion:

$$182.99 : 74.97 = 36 : x. \quad x = 14.74 + \text{grams. Ans.}$$

(4) (a) See Art. 2.

(b) The formula of pure hematite is Fe_2O_3 , its molecular weight is 159.68, and the weight of iron contained in it is 111.68. It therefore contains:

$$111.68 + 159.68 = 69.94\% \text{ Fe. Ans.}$$

(5) See Art. 55.

(6) See Art. 37.

(7) (a) See Art. 20.

(b) See Art. 19.

(8) See Art. 24.

(9) See Art. 65.

(10) See Art. 64.

(11) See Art. 67.

(12) See Art. 45.

(13) See Art. 68.

(14) See Art. 53.

(15) See Art. 55.

- (16) See Art. 50.
- (17) See Art. 60.
- (18) Osmium. See Art. 59.
- (19) See Art. 38.
- (20) (a) See Art. 61.
(b) See Art. 63.

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